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COATINGS FOR THE PROTECTION OF
REFRACTORY METALS FROM OXIDATION

DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus 1, Ohio

COATINGS FOR THE PROTECTION OF
REFRACTORY METALS FROM OXIDATION

by

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to

OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING

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SUMMARY

This report summarizes the current state of the art of coatings to protect refractory metals from oxidation. This field of technology is of vital importance. It is a field of much complexity, and it will require continued research and development if the substantial effort which has been and is being expended on developing structural alloys of the refractory metals is to reach its expected, desired, and required payoff.

Considerable progress has been made in the prevention of the oxidation of the refractory metals by the use of protective coatings. Coatings for molybdenum are the most advanced, followed by those for columbium alloys. Significant progress has been made on coatings for tantalum alloys. Tungsten has received some attention, but the temperature range for its use, >3000 F, precludes any easy solutions. No coatings are available for vanadium alloys. Research and development programs currently are in progress on coatings for these five metals and their alloys.

Silicide, aluminide, and oxide-base materials have shown the most promise as coatings for accomplishing current objectives. Silicide-base coatings have been of most importance for molybdenum and tungsten. Both the aluminide and silicide-base coatings have been of genuine value for the protection of columbium and tantalum alloys.

Pack cementation techniques are being used predominantly in producing silicide coatings. Pack cementation, hot dipping, and paint (slurry dip, spray, brush) and diffused techniques are being used to prepare aluminide-base coatings. Much interest has been exhibited recently in the latter technique.

Most of the effort being devoted to the numerous problems associated with coating systems is Government sponsored. At the present time most of the effort in this field of technology is oriented toward space-vehicle applications.

The present state of the art suggests that a few current coatings will permit use of refractory metals for some space-vehicle applications in the not-too-distant future. However, reliability of production-coating systems has been and continues to be a major problem, although progress is being made in this area.

INTRODUCTION

This report reviews the current status of the art and science of coatings for protecting refractory metals from oxidation. In preparing this report an attempt has been made to: (1) identify the major individual problems which make the over-all protection problem so complex (2) present information and references to major sources of information on materials and methods for producing coating systems, and (3) indicate areas where additional research and development on protective coatings is needed.

In addition to a review of the available literature and research reports, information was obtained from numerous discussions with: (1) research workers dealing with protective-coating problems, (2) coating vendors, (3) engineers who use protected refractory-metal hardware, (4) organizations which have an interest in entering the field of protective coatings, and (5) persons responsible for planning research and development programs to solve some of the major problems of the present-day technology.

The Problem

The group of materials called the refractory metals generally includes those metals with melting points equal to or higher than that of chromium, 3405 F (1875 C). On this basis, there are a dozen refractory metals with widely varying properties and availability. These metals are the subject of intensive research and development because their high-temperature strength properties are required in nuclear-energy applications, advanced aircraft, and space vehicles. Table 1 lists the refractory metals in order of decreasing melting point, together with data on their crystal structure and some of their physical properties. [1]*

Figure 1 shows why the refractory metals are often best suited for structural applications involving temperatures above about 1800 F. [2] Although the nickel- and cobalt-base superalloys have met technological demands very well up to 1800 F, they usually require special techniques to satisfy the higher temperature requirements of nuclear-power generation, atmosphere glide re-entry, rockets, turbojets, and high-Mach ramjets. Also, there appears to be little hope of extending the usefulness of the superalloys into the higher temperature range.

Most high-temperature uses of the refractory metals require operation in an oxidizing atmosphere. Rhodium, chromium, hafnium, and possibly iridium are the only refractory metals which can be termed relatively oxidation resistant. The others suffer from drastically unsatisfactory oxidation resistance in the temperature ranges where their strength properties are required, as shown in Figure 2. [3]

For various reasons, the refractory metals of most importance in current and anticipated technology are tungsten, tantalum, molybdenum, and columbium. [1,4] Except for rhenium and osmium, these four metals as a group are the least oxidation resistant of the refractory metals.

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*References are listed on page 205.

TABLE 1. PROPERTIES OF REFRACTORY METALS[1]

Metals	Melting Point		Boiling Point		Crystal Structure[a]	Density, g/Cm³	Thermal Conductivity, cal/(Cm²)(Cm)(C)(sec)	Electrical Resistivity, microhm-cm At 20 C	Heat Capacity, cal/(g)(C) At 20 C	Coefficient of Linear Expansion, 10⁻⁶ per C near 20 C
	C	F	C	F						
Tungsten	3410	6170	6700	12000	Bcc	19.3	0.48	5.5	0.032	4.5
Rhenium	3180	5755	5630	10100	Hcp	0.17	19.3	0.033	6.7
Osmium	3000	5430	5500	9900	Hcp	22.5	--	9.5	0.031	6.6
Tantalum	2996	542	6100	11000	Bcc	16.6	0.13	13.5	0.033	6.6
Molybdenum	2620	4730	4800	8600	Bcc	10.2	0.35	5.21	0.061	5.4
Iridium	2442	4428	5300	9500	Fcc	22.4	0.35	5.3	0.032	6.5
Columbium	2415	4380	3300	5900	Bcc	8.56	0.125	14.8	0.065	7.1
Ruthenium	2250	4080	4900	8800	Hcp	12.2	--	9.5	0.058	9.6
Hafnium	1975	3585	5400	9700	Hcp[b]	13.36	0.05	30.0	0.035	6.0
Rhodium	1960	3560	4500	8100	Fcc	12.4	0.36	4.7	0.059	8.5
Vanadium	1900	3450	3350	6060	Bcc	6.11	0.074	24.8	0.119	9.7
Chromium	1875	3405	2469	4476	Bcc	7.20	0.16	12.8	0.107	6.2

(a) Bcc designates body-centered cubic. Hcp designates hexagonal close packed. Fcc designates face-centered cubic.
(b) Hcp lattice transforms to bcc at 13 0C.
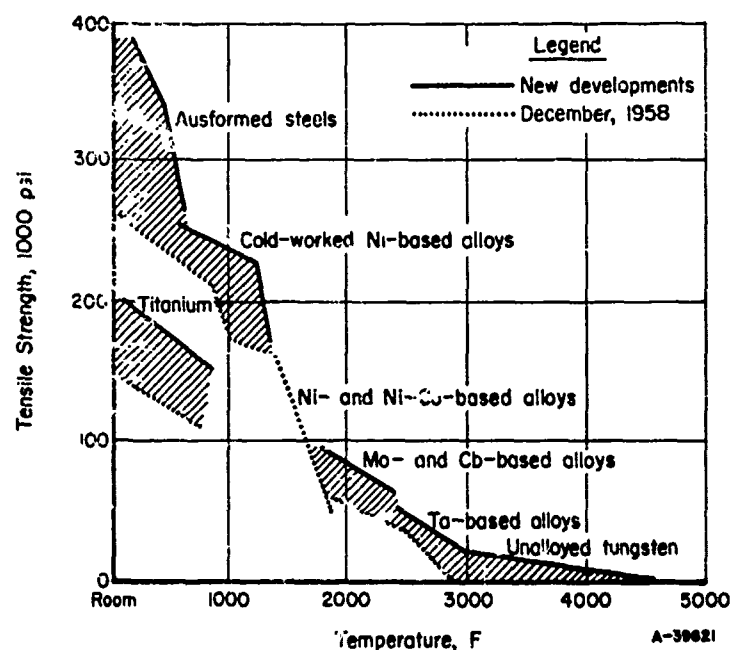
FIGURE 1. HOW STRENGTH LEVELS OF TYPICAL HIGH-TEMPERATURE
STRUCTURAL ALLOYS HAVE RISEN SINCE 1958[2]

Shaded areas indicate the extent of the increase as measured by
tensile strength.
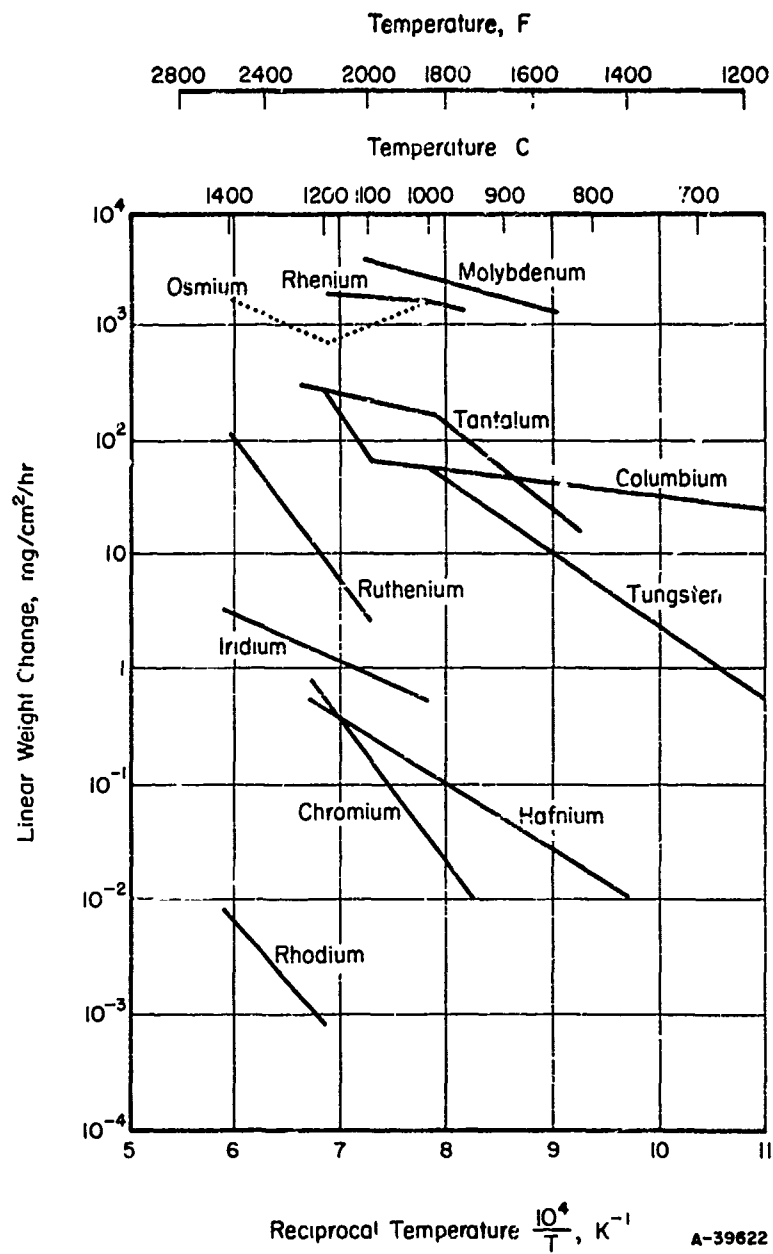
FIGURE 2. CHANGES IN OXIDATION RATE OF REFRACTORY METALS
IN RELATION TO TEMPERATURE[3]

Data for molybdenum, rhenium, osmium, ruthenium, iridium,
and rhodium are weight-loss rates

The most desirable way of overcoming the disadvantages of poor oxidation resistance is through alloying. Considerable improvement in the oxidation resistance of columbium and tantalum has been made by this route. However, those alloys which have satisfactory oxidation resistance do not have satisfactory mechanical and metallurgical properties for most applications. Therefore, it is generally conceded that coatings are required to protect structural refractory-metal alloys from oxidation.

The over-all problem may be stated as one of producing a coating system (coating plus refractory-metal substrate) which will accomplish a desired realistic mission (of which there are several types) with a high degree of reliability.

History of the Problem[5]

No pure metal and no alloy is thermodynamically stable in air even at ambient temperature; as the temperature is increased, the instability of the metals with respect to air increases [25] Most of the metals which are termed oxidation resistant have this quality by virtue of a thin protective oxide coating which rapidly forms on the surface and which prevents or greatly retards the rate of further contact between air and the metal. The principal refractory metals do not form their own protective oxide coatings, hence the problem.

About 1900, the electrical equipment companies became concerned with the protection of tungsten and molybdenum. They provided most of the research effort on the application and use of protective coatings until it became very obvious, in the late 1940's, that the problem was of major interest in the defense effort. Many of the coating materials studied during the early years of research on protective coatings are still under development: noble metals, nickel, chromium, stainless alloys, aluminized and chromized coatings, silicides, alumina, magnesia, and beryllia. This continuing development is not because many of the original problems were not solved, but rather that the environmental conditions and applications become increasingly more severe with time.

Research effort on coatings for columbium and tantalum did not get under way until the late 1950's when these metals became available and their potential as structural materials was recognized.

Today there is a flurry of activity to solve the many problems encountered in providing reliable protective coatings for tungsten-, tantalum-, molybdenum-, and columbium-base alloys. By comparison, only relatively minor effort has been expended on coating vanadium-base alloys which require protection above 1200 F. No work is known to be in progress on coatings for chromium-base alloys which are not expected to require protection, except possibly to reduce nitrogen absorption.

Good structural alloys of the principal refractory metals have been and are being produced by a very substantial research effort. However, these alloys will not assume their prominent role in technology until they can be reliably protected from hostile oxidizing environments.

REFRACTORY-METAL SUBSTRATES FOR COATING SYSTEMS

It is generally agreed that there probably never will be a universal coating which will protect all refractory-metal alloys under all combinations of environmental factors encountered in performing different missions. Each coating will probably be tailored to its substrate to produce a coating system which is specifically designed to accomplish a desired mission.

The first logical step, therefore, in the development or production of a coating system is to select +' substrate which must perform the mission.

Current Alloys and Their Properties

There is considerable research in progress on the development of refractory-metal alloys, particularly those with a columbium or tantalum base. Therefore, alloys which are available today, and for which coatings are being designed, may not be the alloys for which protection is desired in the future.

Table 2 lists alloys of molybdenum, columbium, tantalum, tungsten, and vanadium which are currently in production or in the advanced-experimental-development stage.

Physical and Mechanical Properties

Physical and mechanical properties of these alloys, where available, have been adequately presented in DMIC reports and others to which references have been made in Table 2.

Oxidation Characteristics

General remarks on the oxidation characteristics of the unalloyed refractory metals were made in the Introduction to this report. Figure 2 shows in general how the rate of oxidation changes with temperature.

Columbium- and Tantalum-Base Alloys. Extensive studies have been made of the oxidation behavior of columbium- and tantalum-base alloys. Results of the various research programs have been summarized by Klopp[14] and Schmidt[10] for columbium and tantalum, respectively. Alloys of these metals which have satisfactory oxidation resistance are unsatisfactory as structural materials because of inadequate strength, very poor fabricability, low recrystallization temperature, or other undesirable characteristics.

Molybdenum. Most oxidation studies on metals and alloys have been carried out in static or slowly moving air at atmospheric pressure at temperatures up to about 2200 F. Results from these studies frequently are inadequate for extrapolation to

TABLE 2. ALLOYS OF MOLYBDENUM, COLUMBIUM, TANTALUM, TUNGSTEN AND VANADIUM[1]

Alloy	W	Mo	Ta	Cb	Hf	Ti	Zr	V	C	Other
										Nominal Alloy Composition, weight per cent (Balance Refractory-Metal Base)
Molybdenum-Base Alloys[8]										
Mo-0.5Ti						0.5			0.02-0.05	
TZM						0.5	0.08		0.02-0.08	
TZC						1.25	0.15		0.15	
Mod. TZC						1.27	0.29		0.3	
Mo-0.05Zr							0.054		0.024	
Mo 0.5Zr							0.5		0.02	
Mo-1.5Cb				1.5					0.25	
Mo-25W	25						0.11		0.05	
Mo-0.5TiO2										0.5 TiO2
Columbium-Base Alloys[9]										
F-48	15	5					1		0.1	
F-50	15	5				5	1		0.05	
Cb-7	28					7				
Cb-16	20					10		3		
Cb-65						7	0.8		0.075	0.11 O, 0.02 N
Cb-74	10						5		0.03	0.12 O, 0.02 N
FS-80							0.75			
FS-82			33				0.75			
D-31		10				10			0.06	0.05 O, 0.07 N
D-41	20	6				10				
15-20	15		20							
20-20	20		20							
Cb-Ta-W-Zr	10		24				1			
C-103					10	1	0.5			
Cb-Mo-Hf		5			5					
Cb-W-Zr	10						5			
Cb-Ti						8				
Cb-V-Al								3		3Al
Tantalum-Base Alloys[10]										
Ta-10W	10									
Ta-10Hf-5W	5				10					
Ta-30Cb-7.5V				30				7.5		
Tungsten-Base Alloys[11]										
W-1ThO2										1 ThO2
W-2ThO2										2 ThO2
W-10Mo		10								
W-15Mo		15								
W-25Mo		25								
W-0.38 TaC										0.38 TaC
Vanadium-Base Alloys[12, 13]										
V-50Cb				50						
V-20Cb-5Ti				20		5				

higher t nperatures. Also, in many proposed applications, pressures appreciably less than atmospheric will be encountered. For example, in a hypothetical glide reentry trajectory from 400,000 feet, the temperature at the stagnation point on leading-edge surfaces may range from 2200 to 4500 F at pressures of 0.01 to 500 mm Hg. Under these conditions, and with variable mass flows, changes can occur in the oxidation behavior of the refractory metals, particularly those with volatile oxides such as molybdenum and tungsten.

Modisette and Schryer[15] made a theoretical analysis of the oxidation of a metal forming a volatile oxide which took into consideration gaseous diffusion of oxygen to the surface and an activated reaction at the surface. The result was a rate equation which expressed oxidation rate as a function of temperature, gas properties, flow conditions, and the activation energy at temperatures at which the oxide is gaseous. The oxidation rate of molybdenum subsequently was measured in flowing streams of air and helium-oxygen mixtures at temperatures of 1485 to 2500 F and flow velocities of 1.2 to 6.5 feet per second. The oxidation rate was found to increase with increasing temperature, flow velocity, and diffusivity, in agreement with the results of the analysis.

Wilks[16] investigated the effects of temperature, pressure, and mass flow on the oxidation of molybdenum.. Figure 3 shows the effect of temperature on the rate of oxidation at selected mass flows and pressures; several other graphical correlations were given by Wilks in his paper. Surface-recession-rate equations were derived; but, according to Wilks, they are applicable only for the particular boundary-layer conditions obtained on the test specimens. Fundamental considerations of the oxygen diffusion across the boundary layer, such as was done by Modisette and Schryer[15], are necessary to solve the general problem analytically.

Tungsten. Barth[1] has prepared a summary report on the oxidation of tungsten and tungsten-base alloys.

Perkins and Crooks[18] recently reported results on the low-pressure (1 to 40 mm Hg), high-temperature [1300 to 3000 C (2370 to 5430 F)] oxidation of tungsten which could have a significant bearing on the requirements for protective coatings for this metal. Conclusions reached by these investigators, based mainly on the basis of information presented in Figures 4 through 6, were as follows:

(1) Tungsten oxide volatilizes as fast as it forms in air at temperatures above 2190 F (1200 C) and pressures of 1 to 40 mm Hg; surfaces remain clean and oxidation obeys a linear rate law.

(2) The rate of oxidation from 2370 F (1300 C) to 3180 F (1750 C) in air at pressures of 1 to 40 mm Hg can be calculated from the following relation:

$$K = 14.5\, e^{-\frac{31,500}{RT}}\, p^{0.62},\ g/cm^2/min\ .$$

(3) The dissociation of tungsten oxide is important in the oxidation behavior of tungsten at about 3180 F (1750 C) in air at low pressure; the net rate of metal loss by oxidation decreases with increasing temperature above 3180 F, due to oxide dissociation.
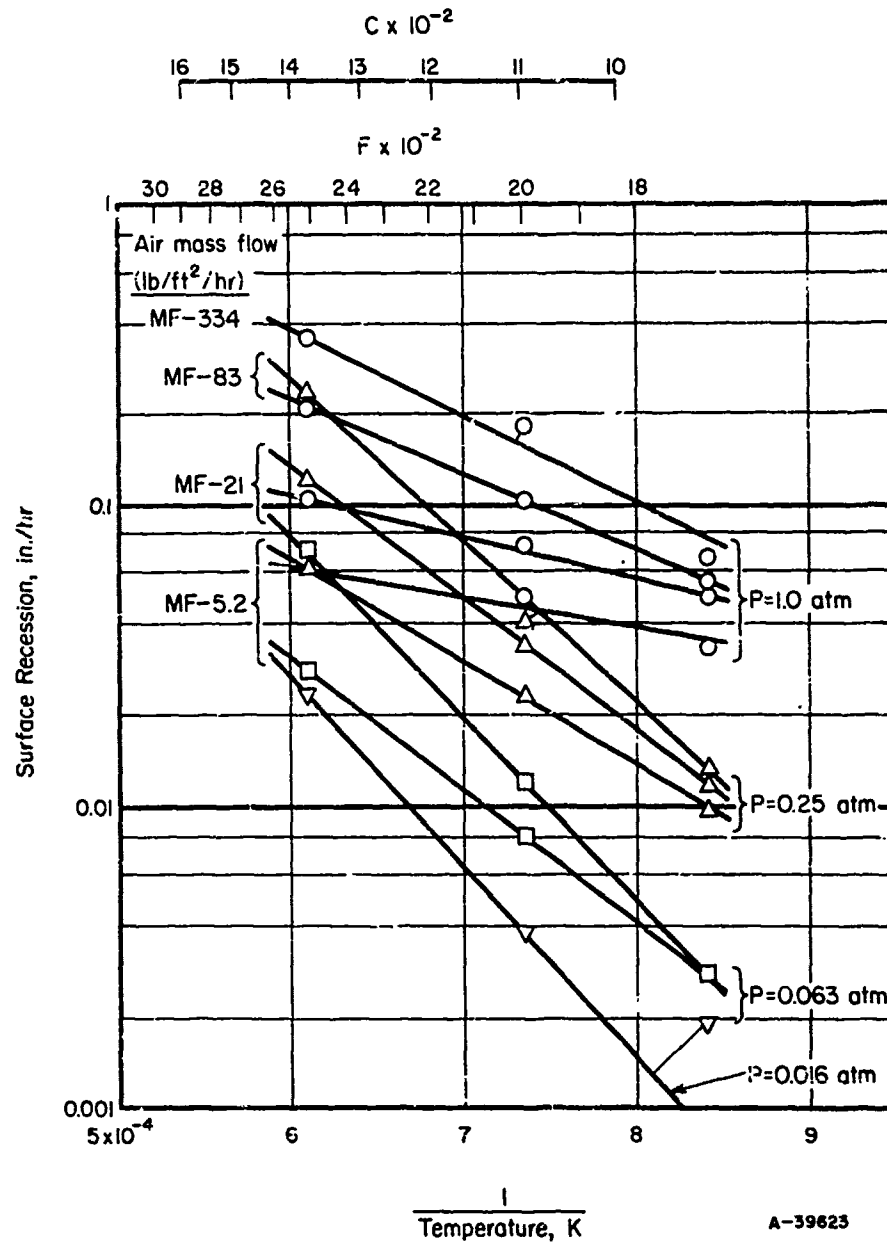
FIGURE 3. EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION OF MOLYBDENUM AT SELECTED MASS FLOWS AND PRESSURES[16]
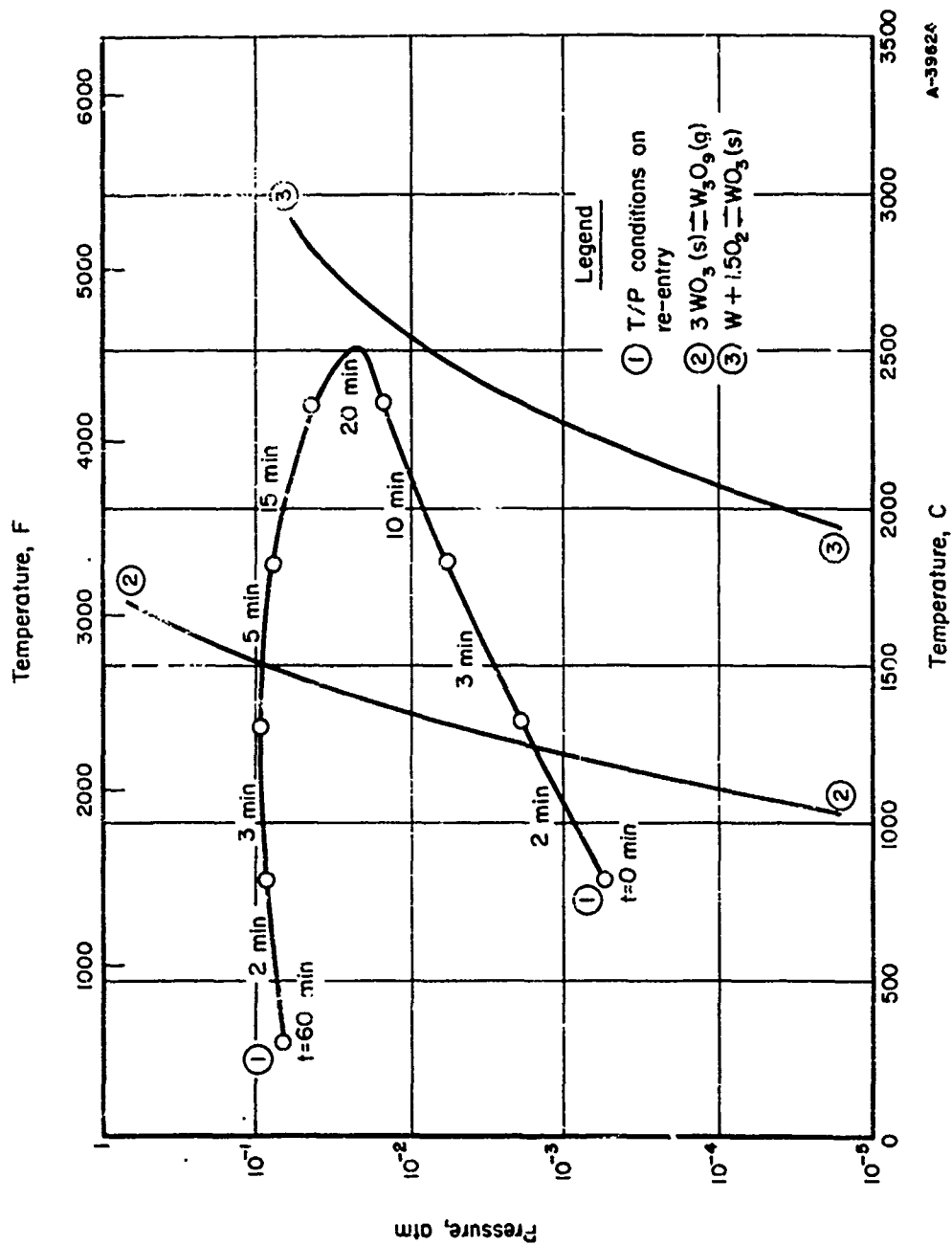
FIGURE 4. RELATION OF TEMPERATURE/PRESSURE/TIME CONDITIONS DURING RE-ENTRY TO TUNGSTEN OXIDATION EQUILIBRIA
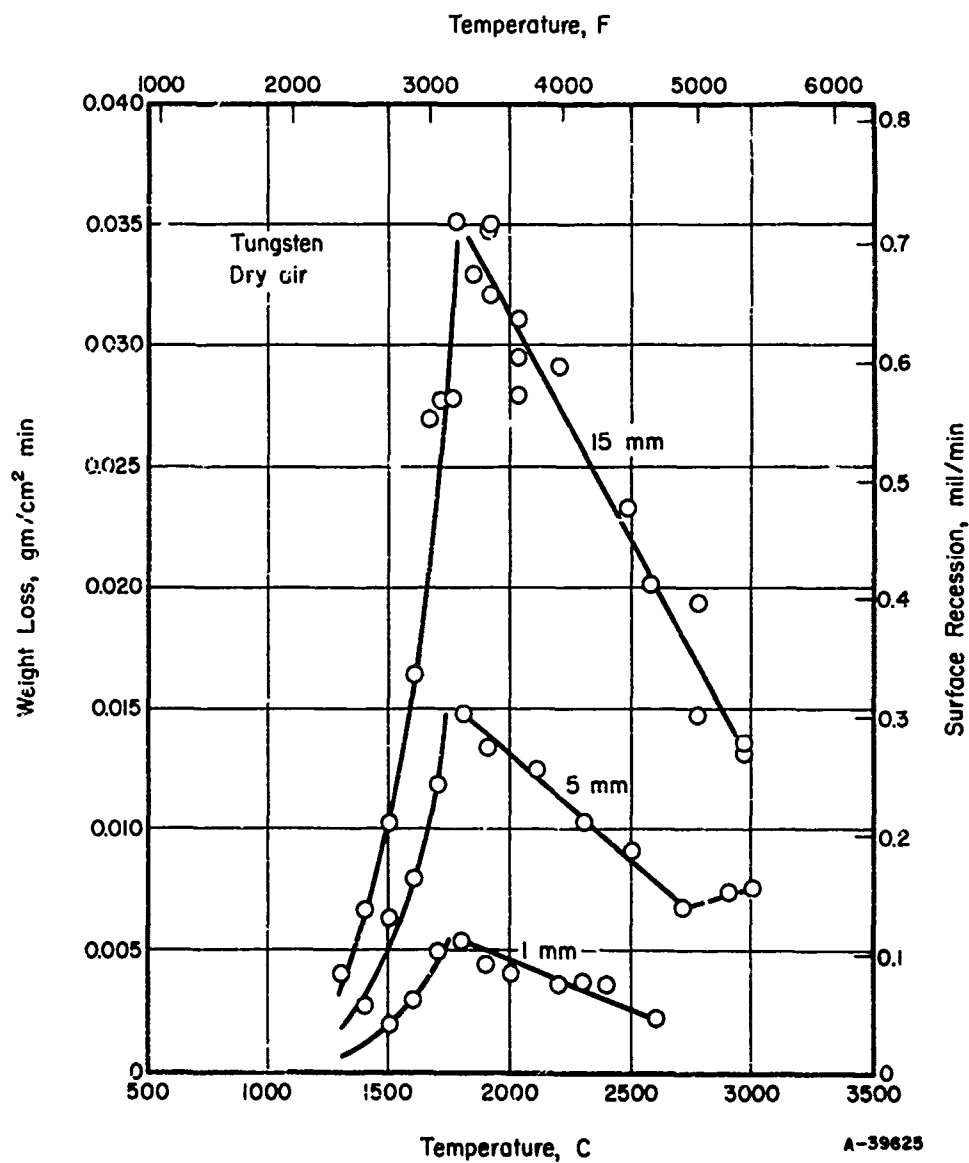
FIGURE 5. RATE OF WEIGHT LOSS OF TUNGSTEN IN AIR AT
1 TO 15 MM Hg PRESSURE FROM 1300 TO 3000 C
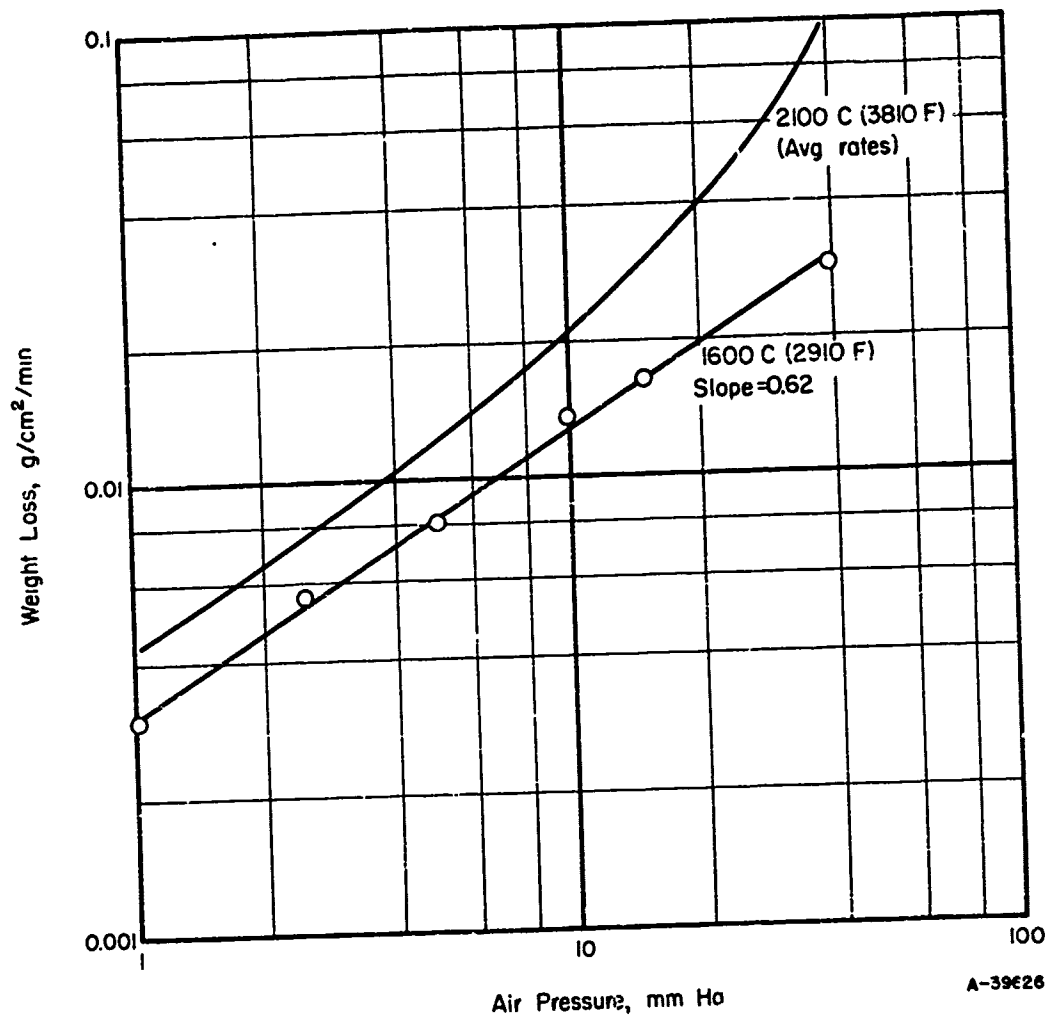
FIGURE 6. EFFECT OF PRESSURE ON OXIDATION RATE OF
TUNGSTEN AT 1600 AND 2100 C

(4) Unalloyed tungsten can be heated in air at pressures below 1.0 mm Hg at all temperatures to its melting point for 1 to 2 hours without excessive surface recession by oxidation.

(5) Oxidation behavior of refractory metals should be analyzed in terms of the specific environment anticipated for a given application; poor resistance to oxidation in normal atmospheres does not preclude consideration for use at high temperatures and reduced pressures.

Vanadium. Rapid scaling of vanadium and vanadium-base alloys in air above 1100 F and the formation of liquid vanadium pentoxide at 1275 F make these materials unsatisfactory for service in air at higher temperatures unless they are protected.

Klicker and Bomberger[19] studied alloys containing elements whose oxides formed high-melting complexes with vanadium oxides to determine whether alloys could be obtained which would form their own protective oxide surface films. Vanadium alloys containing titanium, aluminum, and nickel gave the most refractory scales; and oxide melting points as high as 1950 F were observed. Some of the most promising compositions could be hot worked by rolling and extrusion. Although no alloy was found which had good oxidation resistance in the 1800 to 2100 F temperature range, it was thought that good protection may be possible through natural oxide films from special alloying. However, much additional research and development work is considered necessary before any useful alloys with satisfactory oxidation resistance can be developed.

Other work along this line was reported by Rostoker, McPherson, and Hansen[55].

Importance of Substrate Composition

Much of the current research effort on protective coatings is directed toward coatings formed by diffusion of one or more elements into the surface of the substrate. Obviously the chemical composition of the coating which is obtained by this method depends on the chemical composition of the substrate. The oxidation resistance of the coating, per se, depends on the chemical composition of the coating, and therefore on the composition of the substrate. The oxidation resistance of the coating system (coating plus substrate) depends on the chemical, diffusional, and structural compatibility of the coating and substrate in service, which in turn depend on the chemical composition of the two materials. Therefore, for diffusion-type coatings, it is important that research and development programs be conducted on structural alloys. This is particularly true when columbium-, tantalum-, and vanadium-base alloys are under consideration because, as Table 2 shows, these materials have major alloying additions.

Nondiffusion types of coatings do not depend on the substrate chemistry for their inherent oxidation resistance, and therefore the selection of substrate is less critical from this standpoint. However, the performance of the coating system still depends on the compatibility factors between the coating and substrate, and thus selection of a realistic substrate remains important.

Importance of Substrate Preparation

At least some preparation of the surface of the substrate prior to the application of a coating is usually required to achieve maximum reliability of the coating system. The type of preparation used depends on the substrate (composition and geometry), the coating material, the process of applying the coating, and the service requirements under which the coating system must perform. Usually it is mandatory (1) to round corners and edges to avoid critical stress concentrations and to obtain uniform coverage, and (2) to degrease the substrate.

Much of the information on substrate preparation procedures is proprietary. However, there is quite general agreement that the reliability of the coating system critically depends upon the adequacy of the preparation of the substrate surface. Outlines of procedures which have been used by three different organizations in producing diffusion-type coatings are given below.

Chance Vought[20]

Vought coatings on molybdenum, columbium, and tantalum alloys

(1) Specimen preparation. Deburr and radius all edges and corners Follow by vapor honing.

(2) Specimen cleaning. Degrease, vapor blast, wash in running water, and dry at 250 F for 10 minutes in an oven. Clean white gloves to be used for all handling after degreasing.

(3) Specimen storage. Specimens shall be positioned and packed in the retort (in which the coating is formed) immediately upon removal from the drying oven.

Chromalloy Corporation[21]

W-2 [silicide-base[22]] coating on Mo-0.5Ti

(1) Round corners and edges by grinding, and finish surfaces on silicon carbide paper

(2) Etch with 1-1 HNO_3 for 1.5 minutes

(3) Wash thoroughly with water

(4) Liquid hone

(5) Wash with hot water

(6) Wash with acetone.

General Electric Co.-McDonnell Aircraft Corp. [23]

LB-2 (aluminide-base) coating on Cb alloys F-48 and FS-82

(1) All sheet and plate material which is to be coated
shall have smoothly rounded edges and corners.
Radius of edges shall be half of the sheet thickness.
A 1/8-inch radius shall be maintained on all corners.

   (a) Edge preparation shall be performed prior
to pickling.

   (b) Surfaces prior to pickling shall be free
of visible burrs, nicks, and scratches.

   (c) Surface finish after pickling and honing shall
be 65 rms ± 30 rms.

   (d) Liquid honing shall be used only to remove
oxide scale. Parts having no scale shall
not be liquid honed. Discoloration of the
surface shall be considered as scale.

(2) Vapor degrease as necessary to remove oil and grease.

(3) All paint, crayon, and similar markings must be re-
moved with acetone prior to pickling.

(4) Rinse thoroughly and dry.

(5) Immerse in pickling solution for two minutes.

   (a) Composition

Nitric acid (Conc 42° Bé)	20% by volume
Hydrofluoric acid (70%)	20
Water	60

   (b) Temperature   70 to 100 F.

(6) Rinse thoroughly in cold running water.

(7) Acetone wash and air dry.

(8) Parts shall be handled only with clean white gloves after
processing.

(9) Package in polyethylene bags and seal.

Frequently the proper rounding of corners and edges has been a hand operation
for lack of a better method, and consequently quality control has been difficult to
achieve. Mathauser[24] recently reported that Langley Field, NASA, had been having
poor reliability from a silicide coating on Mo-0.5Ti. This was attributed to inadequate
hand rounding of corners and edges of the laboratory specimens. The problem was
largely overcome by putting the specimens into a rotating drum containing silicon

carbide abrasive and soft copper bolts for agitation. The technique was reported to produce very good and uniform rounding of corners and edges with very little degradation of the flat surfaces.

COATING MATERIALS AND THEIR PROPERTIES

Obviously, materials selected for coatings to protect the refractory metals must be oxidation resistant themselves. (This is a necessary but not a sufficient condition.) All nonoxidic materials are inherently unstable in an oxidizing atmosphere; and, therefore, all coatings will have at least a film or layer of oxide on their exposed surfaces. It is the characteristics of this film of oxide which make materials resistant to gross oxidation. The theory for this type of protection has been reasonably well worked out and has been presented adequately elsewhere. (25-27, 115)

General Material Surveys

Extensive compilations of information on refractory materials in general can be found in References 3, 28, 29, 31-40, 53 and 54. Figure 7 shows the melting points of specific materials within several general classes of r fractory materials.

Borides, carbides, nitrides, and sulfides generally have exhibited poor oxidation resistance. There are some notable exceptions however. Silicon nitride and silicon carbide form protective films of SiO_2. As a result, SiC is reported to have good oxidation resistance to about 2900 F, and Si_3N_4 is reported to be oxidation resistant to 2550 F. Also, Shaffer[30] reported that a 90 mole per cent ZrB_2 - 10 mole per cent $MoSi_2$ solid-solution material resists serious degradation from oxidation for periods of 4 hours at 3540 F, or for shorter periods at higher temperatures. Lewis[67] investigated the deterioration characteristics of 22 materials at a stagnation temperature of 3800 F in a Mach 2 air jet. Materials which showed the best resistance toward deterioration in these tests, as measured by oxidation characteristics, were: silicon carbide-silicon, chromium-28 per cent alumina cermet, and titanium boride-5 per cent boron carbide. Investigations of a similar nature were reported by Trout[237] and Molella[196].

Oxidation resistance with respect to protective coatings for the refractory metals is a completely relative term. Depending on the application, protection may be desired for periods from hundreds of hours to periods of minutes or seconds; the service temperatures involved may range from about 1100 F to 4500 F. Also, an abundance of other environmental factors must be considered in assessing the merits of a material for a protective coating. Therefore, selection of materials for protective coatings should be made with reference to the specific mission which must be accomplished.

Coating-Material Surveys for Specific Refractory-Metal-Base Substrates

Most research programs on protective coatings have at least cursorily surveyed available materials before experiments were carried out to try to produce a good coating system (coating plus substrate). Recent and current surveys will be cited; undoubtedly other rather complete surveys have been made but not published.

FIGURE 7. MELTING POINTS OF SOME REFRACTORY MATERIALS[3]

Molybdenum-Base Substrates

Jaffee's review[41] of protective coating systems for molybdenum and the DMIC report on the subject by Bartlett, Ogden, and Jaffee[42] indicate the variety of materials which have been investigated as coatings for molybdenum; many of these materials probably resulted from surveys conducted over a period of years. Levinstein[43], in reporting the "GE Molybdenum Bucket Story", indicated that approximately 50 coating systems were evaluated. Materials based on chromium, silicon, nickel, precious metals, glasses, and refractory oxides were reported as being foremost among those that had been investigated as coatings for molybdenum.[42]

Columbium-Base Substrates

Klopp[14] and Wlodek[44] cited the variety of materials which had been investigated for columbium-base substrates. Many of these were previously investigated for molybdenum.

Tantalum-Base Substrates

The first phase of a current program[45] on the development of protective coatings for tantalum-base alloys was a survey to identify those materials and compositions which appeared to have the most potential for service to at least 2500 F for a minimum of 6 hours. Available mechanical, physical, metallurgical, and oxidation properties were reviewed for various high-melting-point elements, intermetallic compounds, and oxides. Silicide, aluminide, beryllide, and oxide-base materials were identified as being most attractive for investigation.

Tungsten-Base Substrates

Surveys of potential coating materials for the protection of tungsten from oxidation in the temperature range of 3000 to 3500 F were made at the beginning of the now completed programs which were carried out at New York University[46,47] and the University of Illinois[48,49].

Rhodium with intermediate subcoats of chromium, silicon, and rhenium was selected for investigation as a protective system at 3000 F by the NYU group[46]. In a subsequent phase of this program, tungsten disilicide was selected as the most promising material to investigate as a coating for protection at 3300 F.

Research effort at the University of Illinois was directed primarily toward the use of glassy materials for protection . the temperature range of 3000 to 3500 F.

Two current programs probably will produce additional surveys of potential coating materials for tungsten. The General Telephone and Electronics Co. has a program[50] on "Research Investigation of the Factors Predicating Effectiveness of Protective Systems for Tungsten". The objective of this program is to define and evaluate those variables which are the determining factors in protecting tungsten from atmosphere conditions above 3000 F. Thompson Ramo Wooldridge Inc. has a program[51]

on "Coatings for Protection of Tungsten From Oxidation". The u.., .tive of this program is the development and evaluation of coatings for the protection of tungsten from oxidation at temperatures in excess of 3300 F. The class of materials of primary interest is complex oxides.

Vanadium-Base Substrates

Klicker and Bomberger[19], in their survey of coating materials for the protection of vanadium-base alloys, were interested primarily in oxides and their reactions with vanadium oxides to form high-melting complex oxides. The characteristics of 240 oxide mixtures were studied to identify the most refractory combinations. Melting points of these mixtures ranged from 1225 to above 2500 F. The most refractory mixtures contained one or more of the following oxides: Al_2O_3, Cb_2O_5, CrO_3, NiO, TiO_2, Y_2O_3, and ZrO_2. Twenty-eight of the more refractory oxide mixtures were applied to vanadium sheet, but they appeared to offer little protection as coatings.

A survey of potential coating materials perhaps will emerge from a recently established program by the Bureau of Naval Weapons at the Armour Research Foundation on the "Development of High-Temperature Oxidation-Resistant Protective Coatings for Vanadium-Base Alloys".[238]

Materials of Major Current Interest for Protective Coatings

Classes of materials which have emerged from research and development programs on protective coatings as being of major interest are the oxides (including glasses and complex oxides), intermetallics, platinum-group metals, and cermets

Oxides

Oxidic materials will always be of much importance in the field of protective coatings because, as pointed out earlier, they are the only materials which are inherently stable with respect to the oxidizing environments in which protection must be achieved. Consequently, they must be considered as a component of every operable coating system either (1) in the capacity of the coating itself; (2) as a very thin, adherent, stable oxide film over the major coating (e.g. intermetallics); or (3) as volatile products from the major coating (e.g. platinum-group metals).

Considerable information exists for oxides and, to a lesser extent, oxidic materials in general. Kubaschewski and Hopkins[25] have tabulated melting and decomposition or boiling points, structure, stability, heat of decomposition, and molar volume of oxides. Livey[52] reviewed the high-temperature stability of oxides on the basis of their standard free energies of formation. Runck[28] and Kingery[29] presented extensive compilations of information on oxides for high-temperature applications. Phase diagrams for oxidic materials have been compiled under the auspices of the American Ceramic Society[54]. Table 3 contains some general properties of pure, single, refractory oxides; Table 4 has melting points and densities of complex refractory

TABLE 3. PROPERTIES OF PURE, SINGLE, REFRACTORY OXIDES[a]

Material	Formula	Molecular Weight	Melting Point, C	Boiling Point, C	Density, g/cm^3	Hardness, Mohs' Scale	Other oxides
Aluminum oxide (corundum)	Al_2O_3	101.92	2015	2980	3.97	9	Al_8O_9 ($2Al \cdot 3Al_2O_3$)
Barium oxide (baria)	BaO	153.37	1917	2200	5.72	3.3	BaO_2
Beryllium oxide (beryllia, bromellite)	BeO	25.02	2550	4260	3.03	9	BeO_2
Calcium oxide (calcia, lime)	CaO	56.08	2600	2850	3.32	4.5	CaO_2
Cerium oxide (ceria)	CeO_2	172.13	>2600	--	7.13	6	Ce_2O_3
Chromic oxide	Cr_2O_3	152.02	2265	>3000	5.21	--	CrO, CrO_2, CrO_3
Cobalt oxide	CoO	74.94	1805	--	6.46	--	Co_3O_4, Co_2O_3
Columbium oxide	Cb_2O_3	233.82	1772	--	--	6.5	CbO (Cb_2O_2), CbO_2 (Cb_2O_4), Cb_2O_5
Gallium oxide	Ga_2O_3	187.44	1740	--	5.88[b]	--	Ga_2O
Hafnium oxide (hafnia)	HfO_2	210.6	2777	--	9.68[b]	--	--
Lanthanum oxide (lanthana)	La_2O_3	325.84	2305	4200	6.51	--	--
Magnesium oxide (magnesia, periclase)	MgO	40.32	2800	2825	3.58	6	MgO_2
Manganese oxide (manganosite)	MnO	70.93	1780	4050[c]	5.40	5-6	Mn_3O_4, Mn_2O_3, MnO_2, MnO_3, Mn_2O_7
Nickel oxide (bunsenite)	NiO	74.69	1950	--	6.8	5.5	Ni_3O_4, Ni_2O_3, NiO_2
Silicon oxide (cristobalite)	SiO_2	60.06	1728	2950	2.32[b]	6-7	SiO
Strontium oxide (strontia)	SrO	103.63	2415	3000	4.7	3.5	SrO_2
Tantalum oxide	Ta_2O_5	441.76	1890	--	8.02	--	TaO_2, Ta_2O_4)
Thorium oxide (thoria, thorianite)	ThO_2	264.12	3300	4400	9.69	6.5	Th_2O_7
Tin oxide (cassiterite)	SnO_2	150.70	>1900	1510[d]	7.00	6-7	SnO
Titanium oxide (rutile)	TiO_2	79.90	1840	2227[c]	4.24[b]	5.5-6	Ti_2O_3, Ti_3O_5 ($Ti_2O_3 \cdot TiO_2$), TiO
Uranium oxide	UO_2	270.07	2280	4100	10.96	--	U_3O_8, UO_3
Vanadium oxide	V_2O_3	149.90	1977	3000	4.87	--	V_2O_2 (VO), V_2O_4 (VO_2), V_2O_5
Yttrium oxide (yttria)	Y_2O_3	225.84	2410	4300	4.84	--	--
Zinc oxide (zincite)	ZnO	81.38	1975	1950[c]	5.66	4-4.5	ZnO_2
Zirconium oxide (zirconia)	ZrO_2	123.22	2677	4300	5.56[b]	6.5	ZrO_3

(a) Complied by Runck[28]

(b) Density depends on crystalline form.

SiO_2 (low quartz)	2.65 g/cm^3	TiO_2 (brookite)	4.17 g/cm^3	Ga_2O_3 (monoclinic or rhombic)	5.88 g/cm^3
(low tridymite)	2.26	(rutile)	4.24	(hexagonal)	6.44
(low cristobalite)	2.32	(anatase I)	3.84	HfO_2 (monoclinic)	9.68 g/cm^3
(vitreous)	2.20	ZrO_2 (rhombic, cubic or trigonal)	6.27 g/cm^3	(tetragonal)	10.01
		(tetragonal)	6.10		
		(monoclinic)	5.56		

(c) Decomposes.

(d) Sublimes.

TABLE 4. PROPERTIES OF SOME COMPLEX REFRACTORY OXIDES[a]

Material	Formula	Melting Point, C	Density, g/cm^3
Aluminum silicate (mullite)	$3Al_2O_3 \cdot 2SiO_2$	1830[b]	3.16
Aluminum titanate	$Al_2O_3 \cdot TiO_2$	1855	--
Aluminum titanate	$Al_2O_3 \cdot 2TiO_2$	1895	--
Barium aluminate	$BaO \cdot Al_2O_3$[c]	2000	3.99
Barium aluminate	$BaO \cdot 6Al_2O_3$	1860	3.64
Barium silicate (orthosilicate)	$2BaO \cdot SiO_2$	>1755	5.2
Barium zirconate	$BaO \cdot ZrO_2$	2700	6.26
Beryllium aluminate (chrysoberyl)	$BeO \cdot Al_2O_3$[c]	1870	3.76
Beryllium silicate (metasilicate)	$BeO \cdot SiO_2$	>1755	2.35
Beryllium silicate (phenacite)	$2BeO \cdot SiO_2$	>1750[b]	2.99
Beryllium titanate	$3BeO \cdot TiO_2$	1800	--
Beryllium zirconate	$3BeO \cdot 2ZrO_2$	2535	--
Calcium chromate	$CaO \cdot CrO_3$	2160	3.22
Calcium chromite	$CaO \cdot Cr_2O_3$[c]	2170	4.8
Calcium phosphate (orthophosphate)	$3CaO \cdot P_2O_5$	1730	3.14
Calcium silicate	$3CaO \cdot SiO_2$	1900[b]	2.91
Calcium silicate (orthosilicate)	$2CaO \cdot SiO_2$	2120	3.28
Calcium silicon phosphate	$5CaO \cdot SiO_2 \cdot P_2O_5$	1760	3.01
Calcium titanate (perovskite)	$CaO \cdot TiO_2$	1975	4.10
Calcium titanate	$2CaO \cdot TiO_2$	1800	--
Calcium titanate	$3CaO \cdot TiO_2$	2135	--
Calcium zirconate	$CaO \cdot ZrO_2$	2345	4.78
Cobalt aluminate (cobalt blue)	$CoO \cdot Al_2O_3$[c]	1955	4.37
Magnesium aluminate (spinel)	$MgO \cdot Al_2O_3$[c]	2135	3.58
Magnesium chromite	$MgO \cdot Cr_2O_3$[c]	2000	4.39
Magnesium ferrite (magnesioferrite)	$MgO \cdot Fe_2O_3$[c]	1760	4.48
Magnesium lanthanate	$MgO \cdot La_2O_3$[c]	2030	--
Magnesium silicate (forsterite)	$2MgO \cdot SiO_2$	1885	3.22
Magnesium titanate	$2MgO \cdot TiO_2$	1835	3.52
Magnesium zirconate	$MgO \cdot ZrO_2$	2120	--
Magnesium zirconium silicate	$MgO \cdot ZrO_2 \cdot SiO_2$	1793	--
Nickel aluminate	$NiO \cdot Al_2O_3$[c]	2015	4.45
Potassium aluminum silicate (kaliophilite)	$K_2O \cdot Al_2O_3 \cdot 2SiO_2$	1800	--
Strontium aluminate	$SrO \cdot Al_2O_3$[c]	2010	--
Strontium phosphate (orthophosphate)	$3SrO \cdot P_2O_5$	1767	4.53
Strontium zirconate	$SrO \cdot ZrO_2$	>2700	5.48
Thorium zirconate	$ThO_2 \cdot ZrO_2$	>2800	--
Zinc aluminate (gahnite)	$ZnO \cdot Al_2O_3$[c]	1950	4.58
Zinc zirconium silicate	$ZnO \cdot ZrO_2 \cdot SiO_2$	2078	--
Zirconium silicate (zircon)	$ZrO_2 \cdot SiO_2$	2420	4.6

(a) Compiled by Runck[26].
(b) Incongruent melting.
(c) Spinel-type materials.

oxides; Table 5 gives liquidus temperatures for various oxide combinations; and Figures 8 and 9 show approximate fusion temperatures for several binary oxide

TABLE 5. LIQUIDUS TEMPERATURE (C) FOR VARIOUS OXIDE COMBINATIONS[a]

	Al_2O_3	BeO	CaO	CeO_2	MgO	SiO_2	ThO_2	TiO_2	ZrO_2
Al_2O_3	2050	1900	1400	1750	1930	1545	1750	1720	1700
BeO	1900	2530	1450	1950	1800	1670	2150	1700	2000
CaO	1400	1450	2570	2000	2300	1440	2300	1420	2200
CeO_2	1750	1950	2000	2600	2200	1700 (ca)	2600	1500	2400
MgO	1930	1800	2300	2200	2800	1540	2100	1600	1500
SiO_2	1545	1670	1440	1700 (ca)	1540	1710	1700 (ca)	1540	1675
ThO_2	1750	2150	2300	2600	2100	1700 (ca)	3050	1630	2680
TiO_2	1720	1700	1420	1500	1600	1540	1630	1830	1750
ZrO_2	1700	2000	2200	2400	1500	1675	2680	1750	2700

(a) Compiled by Kingery[29].

combinations based on Cb_2O_5 and V_2O_5, respectively. Table 6 presents melting points of various columbates. Goldschmidt[87] studied binary constitutions of Cb_2O_5 with the oxides of nickel, cobalt, iron, chromium, vanadium, titanium, zirconium, molybdenum, tungsten, magnesium, calcium, strontium, barium, cerium, aluminum, and silicon in varying compositions and in a high- and low-temperature condition. King, Schultz, Durbin, and Duckworth[57] studied four two-component oxide systems involving Ta_2O_5 with Na_2O, MgO, Al_2O_3, or ZrO_2.

Reactions normally occur between pure oxide refractories at temperatures well below the melting point of either constituent with the development of eutectic liquids. Generally, in dealing with ceramic bodies, combinations between basic oxides such as CaO or MgO and acidic oxides such as SiO_2 particularly are to be avoided. However, in protective coating systems, a small amount of softening and promotion of glass formation could be desirable.

Glass formation on the surface of silicide coatings on molybdenum, tungsten, and tantalum has been found to be important for improved oxidation resistance. Glass has been used as an integral part of the coating for columbium[61] and tungsten[48,49]. Reference 62 contains much information on glasses and glass-ceramics.

Silicide, aluminide, and beryllide-base materials are of much prominence in the current technology of protective coatings. Therefore, silica, alumina, and beryllia are oxides of particular interest. Melting points of these three oxides are as follows:

	Melting Point	
Oxide	F	C
SiO_2	3130	1720
Al_2O_3	3705	2040
BeO	4620	2550

Other properties of silica[28,63], alumina[28,63,64], and beryllia[28,63,65,66] have been summarized elsewhere.
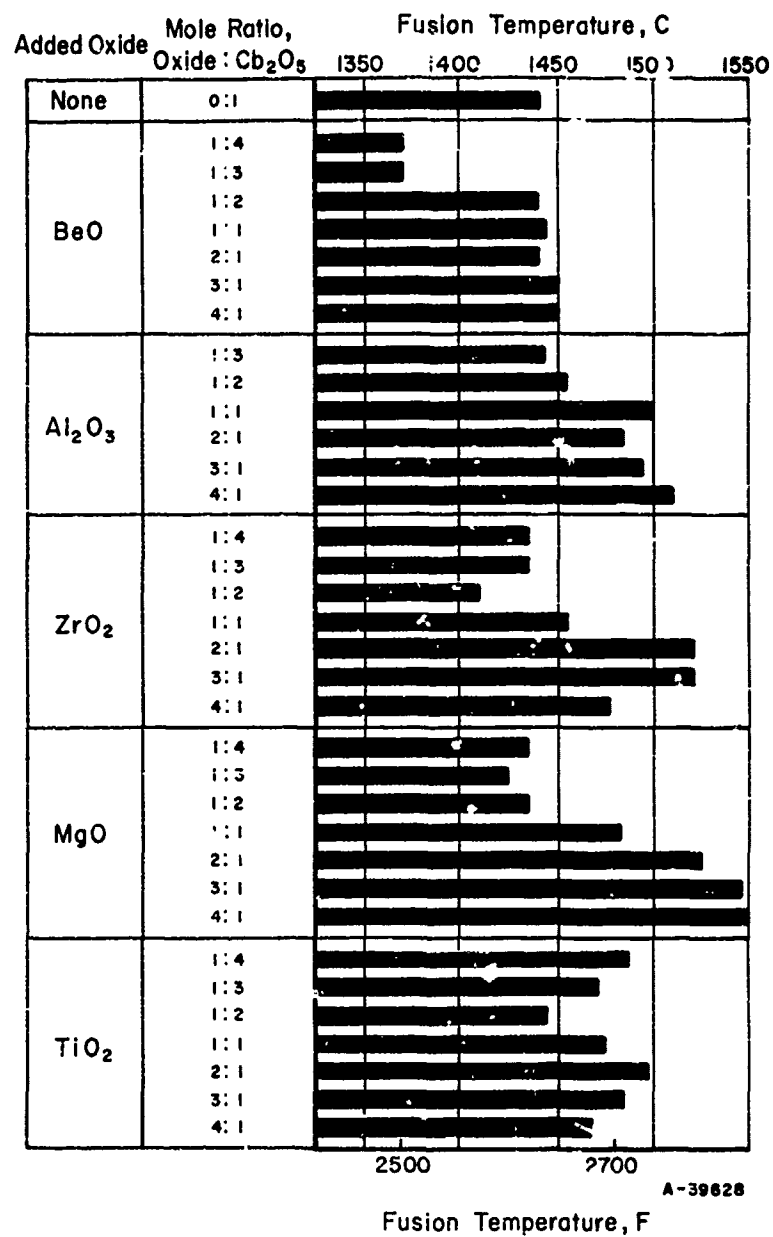
FIGURE 8. APPROXIMATE FUSION TEMPERATURES OF
Cb₂O₅ – BASE CERAMICS[58]
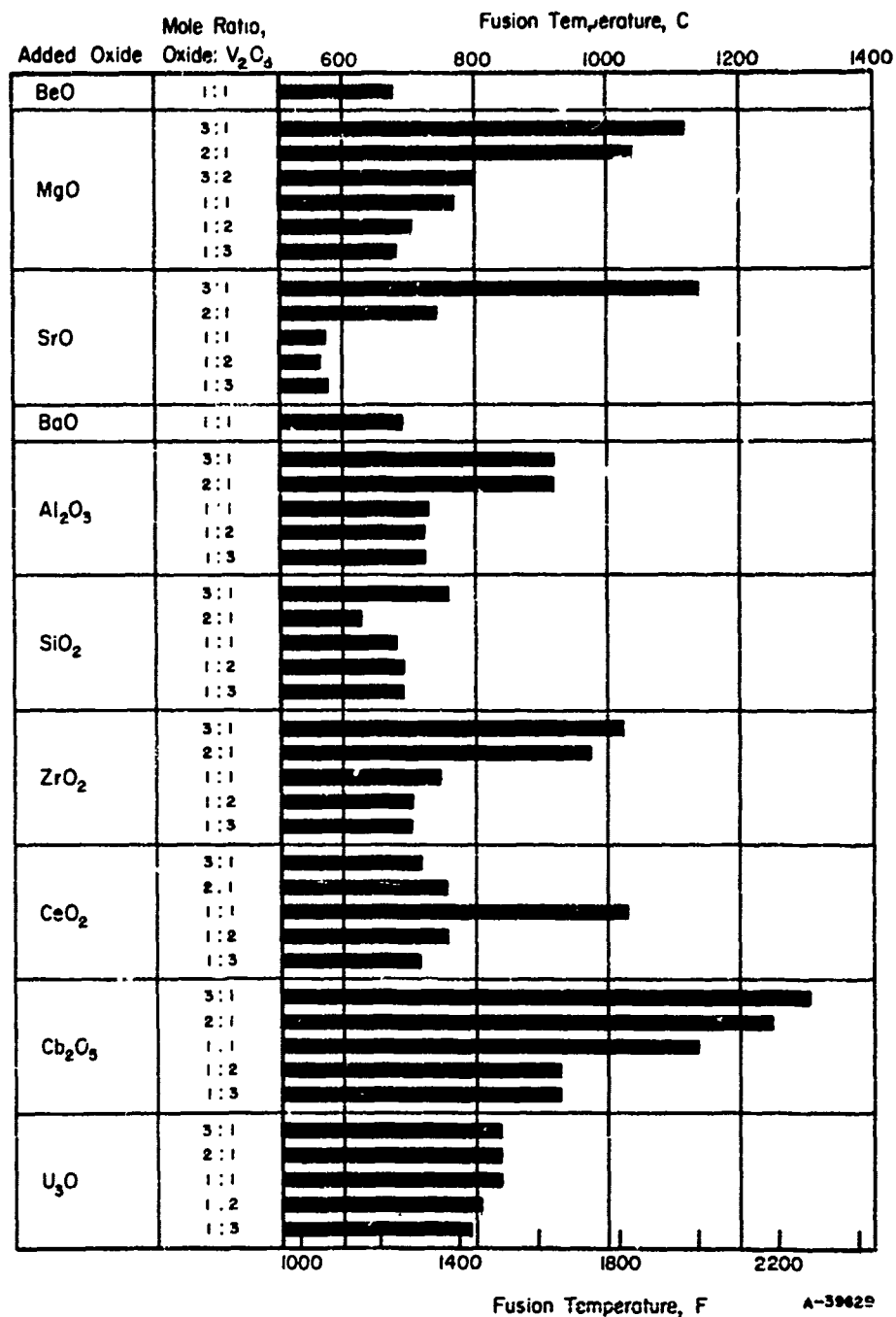
FIGURE 9. APPROXIMATE FUSION TEMPERATURES OF BINARY MIXTURES CONTAINING V_2O_5[60]

TABLE 6. MELTING POINTS OF VARIOUS COLUMBATES[59]

Compound or Solid Solution	Approximate Melting Points		
	F	C	Color
Cb_2O_5	2625	1440	White to yellow
$MgO \cdot Cb_2O_5$	2670	1480	Pink to orange
$2MgO \cdot Cb_2O_5$	2750	1510	Pink to orange
$3MgO \cdot Cb_2O_5$	2805	1549	Pink to orange
$4MgO \cdot Cb_2O_5$	2805	154''	Pink to orange
$Al_2O_3 \cdot Cb_2O_5$	2750	1510	White
$ZrO_2 \cdot 3Cb_2O_5$ (eutectic)	2625	1440	Cream to gray-white
$6ZrO_2 \cdot Cb_2O_5$	3045	1675	Cream to gray-white
$TiO_2 \cdot Cb_2O_5$	2715	1490	Yellow to green
$TiO_2 \cdot 3Cb_2O_5$	2700	1480	Yellow to green
$BeO \cdot 4Cb_2O_5$	2490	1365	--
$BeO \cdot 3Cb_2O_5$	2490	1365	--
$BeO \cdot 2Cb_2O_5$	2635	1445	--
$BeO \cdot Cb_2O_5$	2635	1445	--
$Cb_2O_5 \cdot V_2O_5$	2055	1125	Gray
$Cb_2O_5 \cdot V_2O_4$	3290	1810	Black
$LiCbO_3$[a]	1875	1024	White
$NaCbO_3$[a]	2200	1205	Cream
$Na_2Cb_4O_{11}$[a]	2250	1232	Cream
$KCbO_3$[a]	2000	1094	White
$K_2Cb_4O_{11}$[a]	2200	1205	Cream
$BaCbO_3$	2400	1315	Gray-blue
$BaCb_2O_7$	2450	1344	Gray-white
$SrCbO_3$	2600	1427	Gray
$SrCb_2O_7$	2500	1370	Gray
$CaCbO_3$	2500	1372	Gray
$CaCb_2O_7$	2500	1372	Gray
$2ZnO \cdot Cb_2O_5$	2100	1149	Tan
$3CdO \cdot Cb_2O_5$	2450	1344	--
$2CdO \cdot Cb_2O_5$[b]	2640	1450	Tan

(a) Known to be hygroscopic.
(b) Sublimes above 1200 C.

Special mention should be made of beryllia. This oxide has great thermal stability, unusually high thermal conductivity, very low electrical conductivity, a moderate and uniform thermal expansion, and is very resistant to thermal shock. It is relatively weak at low temperatures, but its mechanical properties remain fairly constant with temperature to about 2900 F, and at this temperature, it is one of the strongest oxides in compression.[28] Beryllia has two major drawbacks, however. First, it is vulnerable to attack by water vapor. The reaction

$$BeO(s) + H_2O(g) \rightarrow BeO \cdot H_2O(g)$$
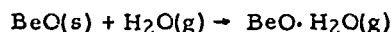
becomes quite a serious problem above 2280 F if the dew point of the surrounding air becomes high. Secondly, beryllium and its compounds are toxic. Contact with the skin and inhalation of dust or fumes should be avoided. Permissible tolerance levels of beryllia dust in the atmosphere and precautions for handling beryllia in a plant or laboratory should be established by competent medical authority and observed rigorously.[66]

Compilations of thermodynamic data for oxides and oxidic materials can be found in References 52 and 68-73 Methods for estimating thermodynamic data are given in References 74 and 75.

As temperature requirements for oxidic materials go higher and higher, dissociation and volatility of even the refractory oxides become important. References 29, 52, 72, 73, 76-82, and 204 give summaries and compilations of data on this aspect. $Cr-Cr_2O_3$ and $Si-SiO_2$ are of importance in current coating systems. Volatility of Cr_2O_3 has been studied by Wang[83] et al. and Grimley[84] et al. Kaiser and Breslin[85] and Wagner[86] studied equilibria in the silicon-oxygen system.

Intermetallics

Surveys of intermetallics are presented in References 28, 29, 32-34, 36, and 262. Property data are continuing to be generated by Paine et al.[37,38]

Paine, Stonehouse, and Beaver[36] presented a comprehensive literature survey of binary intermetallic systems which were believed to hold the greatest promise of containing high-melting intermetallic compounds. A total of 798 binary systems were included in the literature survey. Data tabulated for all compounds melting above 2550 F included, where available, physical properties (such as crystal structure, melting point, hardness, strength, and impact resistance) and oxidation resistance. In general, very few data aside from melting points were contained in the literature.

Intermetallic compounds from 35 binary metallic systems subsequently were prepared, fabricated into oxidation-test specimens, and tested for oxidation resistance in dry air at 2300 F. Compounds studied were aluminides, beryllides, silicides, germanides, zirconides, and numerous miscellaneous compounds. Data for promising compounds for high-temperature applications, as compiled by Paine et al., are given in Table 7. A few compounds were tested at 2500 F, results from these tests are given in Table 8.

TABLE 7. PROMISING COMPOUNDS FOR VERY-HIGH-TEMPERATURE APPLICATIONS

Compound	Melting Point, F	Density$^{(a)}$, g/cm^3	Oxidation Resistance After 100 Hours at 2300 F		
			Sample Density, per cent of absolute	Weight Gain, mg/cm^2	Calculated Penetration, mils
CbAl$_3$	>2550	4.57 (X)	90	2.8	0.4
TaAl$_3$	>2730	6.92 (X)	92	7.1	0.9
CrBe$_2$	3340	4.34 (X)	96	2.4	0.3
MoBe$_{12}$	~3100	3.03 (X)	94	2.6	0.2
Cb$_2$Be$_{17}$	>3000	3.28 (P)	94	2.6	0.3
CbBe$_{12}$	>2800	3.04 (SP)	95	1.7	0.2
TaBe$_2$	~3350	9.79 (P)	90	4.1	0.4
TaBe$_{12}$	>3000	4.18 (X)	90	18.0	2.1$^{(b)}$
TiBe$_2$	~2600	3.21 (SP)	98	5.2	0.6
TiBe$_{12}$	>2600	2.26 (X)	94	3.0	0.4
"WBe$_5$"	~3250	6.91 (SP)	93	5.1	0.6
Zr$_2$Be$_{17}$	2790	3.15 (SP)	96	9.1	1.0
ZrBe$_{15}$	2910	2.72 (X)	93	7.8	1.0
Cr$_3$Si	3190	6.46 (X)	91	7.3	0.8
Ti$_5$Si$_3$	3670	4.32 (X)	91	2.3	0.2
"TiSi"	3200	~4.25 (SP)	94	3.4	0.3
TiSi$_2$	~2700	4.12 (X)	96	2.2	0.2
TaCr$_2$	3540	11.23 (X)	82	46.3	5.1

(a) Density reported is that considered most reliable for the material tested.

    (X) = X-ray density of compound.

    (P) = Pycnometric density of compound preparation.

    (SP) = Pycnometric density of fabricated material after powdering.

(b) This sample showed a weight gain of 17.0 mg/cm^2 after 5 hours at 2300 F, corresponding to a calculated penetration of 2.0 mils.

TABLE 8. OXIDATION RESISTANCE OF INTERMETALLIC COMPOUNDS IN DRY AIR AT 2500 F (100-HOUR TEST)

Compound	Sample Density, per cent of absolute$^{(a)}$	Weight Gain, mg/cm^2	Calculated Penetration, mils
CrBe$_2$	93 (X)	24.9	2.8
MoBe$_{12}$	94 (X)	4.5	0.4
CbBe$_{12}$	95 (SP)	17.1	2.1
TaBe$_{12}$	90 (X)	12.7	1.5
TiBe$_{12}$	90 (X)	8.3	1.0
Ti$_5$Si$_3$	91 (X)	10.1	1.0

(a) (X) = Based on X-ray density of compound.

    (SP) = Based on pycnometric density of fabricated specimen after powdering.

Conclusions from the work were as follows*:

(1) The following compounds have good oxidation resistance in dry air at a temperature of 2300 F (based upon 100-hour tests):

$CbAl_3$	$TiBe_2$
$TaAl_3$	$TiBe_{12}$
$CrBe_2$	"WBe_5"
$MoBe_{12}$	Zr_2Be_{17}
Cb_2Be_{17}	$ZrBe_{13}$
$CbBe_{12}$	Cr_3Si
"$ReBe_6$" and "$ReBe_{16}$"	Ti_5Si_3
"$TaBe_2$"	"$TiSi$"
Ta_2Be_{17}	$TiSi_2$
$TaBe_{12}$	$TaCr_2-Ta_3Cr_2$

(2) The following compounds are considered to be the most worthy of further study:

$CbAl_3$	"$TaBe_2$"
$TaAl_3$	Ta_2Be_{17}
$CrBe_2$	$TaBe_{12}$
$MoBe_{12}$	$TiBe_{12}$
Cb_2Be_{17}	$ZrBe_{13}$
$CbBe_{12}$	Cr_3Si
	Ti_5Si_3

(3) Compounds which were tested but lacked the necessary oxidation resistance or stability at 2300 F are:

Mo_3Al	$CbBe_3$	"$CrSi$"
"$MoAl_3$"	$PdBe$	$LaSi_2$
Cb_3Al	$PdBe_5$	Cb_5Si_3
"Cb_2Al" (single phase not tested)	$PtBe$	$CbSi_2$
	$PtBe_5$	$TaSi_2$
$ZrAl_3$ (and other Zr-Al compounds)	Mo_3Ge	$ZrCr_2$
	Cb_5Ge_3	$ZrMo_2$ (free Mo present)
$CeBe_{13}$	Cb_2Ge	
$CrBe_{12}$ (fair resistance but low mp)	Ta_5Ge_3	"$ZrNi_3$"
	Zr_5Ge_3	"$ZrNi_4$"
$LaBe_{13}$	$ZrGe$	"Zr_2Sn"
$MoBe_2$	$CeSi_2$	$Cb_2Cr_3-CbCr_2$
$CbBe_2$	"Cr_5Si_3"	$Cb_3Fe_5-Cb_3Fe_7$
		$Ta_3Fe_5-Ta_3Fe_7$

Miscellaneous observations and comments of interest, made by the personnel of Brush Beryllium Co., were as follows:

(1) NiAl and Ni3Al have shown excellent oxidation resistance and strength at temperatures up to 2010 F, but above this temperature, oxidation becomes appreciable.

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*Because of the large amount of work which already has been done on molybdenum silicides, Paine, et al., did not include these compounds in their studies. However, $MoSi_2$ should be included as being worthy for definite consideration.

(2) The compound TiAl has a Rockwell A hardness of 75 and shows a transverse rupture strength of 100,000 psi at 1830 F. The oxidation resistance is good at 1830 F, but is not satisfactory in the 2300 to 2500 F range.

(3) A specimen of $TaAl_3$ which had been oxidized at 2300 F, had a tough sintered scale which was very tenacious. This compound shows excellent promise, based on oxidation resistance, for applications at very high temperatures.

(4) $CbAl_3$ has a tetragonal structure with a = 5.427 A and c = 8.585 A. Density is 4.54 g/cm^3. It was observed that tungsten carbide-tipped tooling could not be used to machine $CbAl_3$, and a silicon carbide cutoff wheel cut extremely slowly. A specimen of $CbAl_3$ which had been oxidized at 2300 F had a very thin, tough oxide scale, which appeared sintered and could not be easily removed.

(5) In general, "line" compounds with a narrow range of homogeneity could be expected to be more brittle, while those compounds with a wide range of homogeneity could be expected to be able to withstand more deformation without fracture. Those compounds with a large amount of one element, such as the MBe_{12} compounds, could also be more liable to withstand deformation without fracture. In this regard, it is interesting to note that Cb_2Be_{17} is structurally very similar to $CbBe_{12}$. In one instance, a $CbBe_9$ composition gave the $CbBe_{12}$ structure, indicating that there may be a fairly wide field of homogeneity in the MBe_{12}-type compounds.

(6) Cb_2Cr_3 and Ta_2Cr_3 are reported with a wide range of homogeneity. The oxide formed at 2300 F on Cb_2Cr_3 was fairly loose and powdery, and apparently not protective at 2300 F. The oxide on Ta_2Cr_3 was not sintered appreciably, and, for the most part, was nonadherent and flaked easily. However, optimum test specimens of Ta_2Cr_3 were not obtained, and the fact that oxidation resistance was fairly good even though the oxide scale did not appear to be protective suggests that additional study of this material should be made.

(7) The compound TiSi was not tested as such, but only as a mixture of several titanium silicides. However, all compositions and mixtures of titanium silicides showed good oxidation resistance.

(8) $MoSi_2$ has been reported as being resistant to oxidation at temperatures up to about 3100 F (3 micrograms weight loss/cm^2/hr at 2850 F in air). It has been reported, however, that at lower temperatures the oxidation resistance is considerably less than at the higher temperatures. All of the silicide compounds of molybdenum are quite brittle at room temperature. The disilicide has shown good strength at elevated temperatures (100-hour stress-rupture value of 8,500 psi at 2000 F). Its primary drawback is creep at temperatures exceeding about 1800 F.

(9) Kieffer reported that all silicides of columbium (and vanadium) are brittle and lack oxidation resistance. Paine et al. obtained the following oxidation data for $CbSi_2$ (93 per cent of theoretical density) which might have contained some carbide:

Time at 2300 F, hr	Weight Gain, mg/cm^2
25	4.7
100	141 (completely oxidized)

(10) In arriving at a fair estimate of the resistance of a particular compound, it was necessary for Paine et al. to take into account the degree of porosity present in the actual test specimen, because weight-gain figures do not represent the true oxidation resistance of a material in the presence of such porosity. The nature of the weight gain-versus-time curve is believed to be quite important in this respect, in that initial'y high weight gains may be observed, but after a time at temperature, the further weight gain may be quite low, indicating that surface porosity has become filled with oxide and that a truly protective coat has been established on the sample. This was shown markedly in the case on the $TaBe_{12}$ specimen which contained 10 per cent porosity. The sample gained 17.0 mg/cm^2 the first 5 hours at 2300 F and only an additional 1.0 mg/cm^2 the last 95 hours. A similar change in rate was noted in a 2500 F test.

The objective of the above work by Brush Beryllium was the development of intermetallic-compound materials with useful properties in the temperature range of 2300 to 3000 F and a service life as determined by oxidation resistance of 100 hours. In pursuing this objective, experimental work was concentrated on $MoBe_{12}$, $CbBe_{12}$, $TaBe_{12}$, $TiBe_{12}$, and $ZrBe_{13}$. Properties of these materials are summarized in Table 9.

A new objective evolved for the continuation of the Brush program, namely, to provide materials for use where very high temperatures are encountered for relatively short periods of time (up to 10 hours). Studies pursuant to this objective showed that $TaBe_{12}$, Ta_2Be_{17}, Hf_2Be_{21}, Hf_2Be_{17}, $MoSi_2$, $TaSi_2$, and WSi_2 possessed sufficient oxidation resistance at 2900 F to be given more advanced evaluations.[37,38]

Aluminides. Paine et al.[36] reviewed aluminides as indicated above. The only aluminides considered to have merit for the 2300 to 3000 F, 100-hour objective were $CbAl_3$ and $TaAl_3$. Considerable work has been and is being done on utilizing aluminide-base coatings for the protection of columbium and tantalum-base alloys from oxidation.

Low-temperature (~1000 to 1500 F) "pest" failure has been observed in unmodified aluminide coated columbium and tantalum similar to the "disilicide pest" described in the next section of this report.[209]

TABLE 9. SUMMARY OF INTERMETALLIC-COMPOUND PROPERTIES[37]

Compound:	$ZrBe_{13}$	$CbBe_{12}$	$TaBe_{12}$	$MoBe_{12}$	$TiBe_{12}$
Melting point, F	3500	3070	3360	~3000	>2910
X-ray Density, g/cm^3	2.72	2.91	3.18	3.03	2.26
Max. 100-Hour Service Temp in Dry Air, F	2900	2700	2800	2700	2600
Modulus of Rupture, psi					
2300 F	36,000	39,000	56,000	42,000	--
2500 F	36,000	39,000	43,000	30,000	--
2750 F	25,000	18,000	26,000	13,000	--
Young's Modulus, 10^6 psi					
2300 F	25	25	24	15	--
2500 F	20	15	14	12	--
2750 F	10	10	10	1	--
Thermal Conductivity, Btu hr^{-1} ft^{-2} ft F					
1600 F	21.0	17.9	11.0	18.2	--
2600 F	20.8	19.0	10.5	17.5	--
Specific Heat, Btu/(lb)(F)					
1600 F	0.41	0.40	0.28	0.41	--
2600 F	0.46	0.43	0.30	0.45	--
Thermal Expansion, 68 - 2600 F, in./in./F	9.8×10^{-6}	9.2×10^{-6}	8.3×10^{-6}	--	--

Beryllides. These materials have been studied systematically and extensively by Paine et al.[36-38] Lewis[88] recently reviewed the beryllides. He concluded that the intermetallic compounds formed between beryllium and the transition-metal elements are hard, toxic, low-density materials with good-to-excellent oxidation resistance and attractive nuclear properties. They are, without known exception, quite brittle, even at temperatures approaching 2000 F. Several beryllides exist with melting points above 3000 F, although none are known which melt above 3700 F. They retain their mechanical strength to rather high temperatures — Zr_2Be_{17} has a rupture modulus of 24,000 psi at 2750 F. Because the protective oxide which forms upon exposure to air is BeO, the beryllides probably will have to be protected against attack by the water vapor in air.

Beryllides have been investigated as protective coatings, particularly with respect to columbium and tantalum-base substrates. The high thermal expansion of beryllides, relative to the refractory metals, and rapid interdiffusion can be sources of difficulties depending upon the system and the parameters of the test or service environment.

Silicides. A very large amount of research and development effort has been expended on silicide-base materials as protective coatings for the refractory metals. Much of the effort on silicide-base coatings for columbium, tantalum, and tungsten has been an offshoot from work with silicide-base coatings for molybdenum.

Reviews and compilations of data on silicides in general can be found in References 28, 29, 33, 36, and 89-92. Additional information on the molybdenum-, tungsten-, and tantalum-silicon systems is given in References 37, 47, 82, and 93-96 for molybdenum, References 37, 47, and 96 for tungsten, and Reference 37 for tantalum.

The molybdenum-silicon system, and molybdenum disilicide in particular, has been under investigation for a considerable period of time, both in bulk form and as protective coatings. Yet, bulk $MoSi_2$ is not well understood and is the subject of continuing research.[82,96] Neither the rate nor detailed mechanism of oxidation is well established.

It is believed that the excellent oxidation resistance of $MoSi_2$, WSi_2, SiC, and Si_3N_4 is derived from the formation of nearly pure silica as the only condensed-phase oxidation product.[92] In each reaction, more than enough silica is produced to occupy the volume of the silicide that has reacted. Diffusion of oxygen and metal ions in pure silica is slow. Hence, excellent oxidation resistance results.

A phenomenon called the "disilicide pest" has been observed for both $MoSi_2$ and WSi_2.[47,48,92,96] Poor oxidation resistance is exhibited in the temperature range where the pest occurs. Although the phenomenon is not well understood, it has been suggested that it is caused by contamination of the glassy SiO_2 scale formed during oxidation, by MoO_3 in the case of $MoSi_2$ or by WO_3 in the case of WSi_2. In the temperature region of the pest occurrence, the vapor pressure of the volatile oxide is considered to be insufficiently high to allow its rapid removal from the SiO_2; thus contamination results. It is interesting to note that the temperature range for $MoSi_2$ pest has been reported as extending from 600 to 930 F up to 1300 to 1800 F. Tentatively, the temperature range for WSi_2 pest begins at 1200 F and ends at about 2280 F. The

difference in the upper limit in the two cases correlates with the difference in vapor pressure of the two oxides, MoO_3 and WO_3; the vapor pressure of WO_3 is appreciably lower than that of MoO_3 at any given temperature. The upper temperature limit for pest formation is roughly the same as the temperature at which the oxides have a vapor pressure of 10^{-3} atm, namely 1440 and 2350 F for MoO_3 and WO_3, respectively. Additional evidence for the contamination theory comes via silicon carbide and silicon nitride. Both compounds yield silica as the only condensed-phase oxidation product, and both have excellent oxidation resistance.

On the other hand, Searcy[92] cited several lines of evidence to suggest that the oxide product layer on $MoSi_2$ is not simply silica. Also, it has been reported informally that pure $MoSi_2$ (free of other elements and stoichiometrically exact) does not exhibit the pest.

Silicon carbide might also be called carbon silicide. A comprehensive review of this material was made by Brown[97]. Jorgensen, Wadsworth, and Cutler[98-100] carried out detailed oxidation studies on silicon carbide, and Davis, Anthrop, and Searcy[101] studied its dissociation.

The development of hexaboron silicide (B_6Si) and tetraboron silicide (B_4Si) for use at high temperatures was recently announced.[102] These materials form an amorphous phase, probably a silicon-boron-oxygen glass, during initial oxidation which gives them an oxidation-resistant protective coating for at least as long as 65 hours at 2500 F. Thermal-shock resistance was reported as being exceptionally good. No cracking was observed after 50 cycles between 2000 F and room temperature in air. Also, no cracks occurred when the materials were heated to 2000 F and quenched in water. Tetraboron silicide disproportionates to hexaboron silicide and silicon at high temperatures.

Platinum-Group Metals

As part of a broad research program on the high-temperature properties and alloying behavior of the refractory platinum-group metals, Douglass, Holden, and Jaffee[103] prepared a comprehensive literature survey in 1959. Results of the survey and subsequently obtained experimental results were summarized by Jaffee, Maykuth, and Douglass in 1960.[104] A final report will summarize all of the information generated in the research program.[105]

Recent studies have been made of the vapor pressure of platinum[107], palladium[106,107], iridium[81,82], and rhodium[81,82]. The behavior of the platinum-group metals in high-temperature oxidizing atmospheres also has been under investigation recently.[104,105,108-114,265]

Platinum, palladium, iridium, and rhodium have been and are being considered in protective-coating systems. Potential difficulties, depending upon the coating and substrate compositions and the intended service, could arise from thermal-expansion mismatch, formation of brittle intermetallics at the interface, and oxidation of the substrate by diffusion of oxygen through the coating.

Cermets

Considerable research and development has been conducted on cermets for use as singular solid bodies. Much of this effort was concentrated on making hardware. The state of the art of cermets is well presented in References 28, 115-122, and 263.

Relative to other types of materials, the cermets have received very little attention as protective coatings. There is current interest in this area of application, particularly for service conditions involving ultrahigh temperatures and severe erosion for short periods of time.

Properties for Consideration in Selecting Materials for Coatings

A protective coating generally must maintain protection from oxidation through one or more of the following conditions: thermal cycling, thermal shock, tension, compression, creep, bending, shear, alternating mechanical stresses, impact, erosion, hypersonic air flow, acoustical vibrations, ultrahigh vacuum, and radiation of various kinds and intensities. Some of these environmental factors are not well defined at the present time.

For many materials of interest as protective coatings, complete property evaluations on bulk materials are not available. Even where such data are available, it may not be possible to extrapolate the bulk data to (or interpret for) performance of a thin layer of the material bonded to a refractory-metal substrate. The problem is compounded because most of the materials of interest as protective coatings for realistic missions are brittle.

For these reasons many materials have been selected as candidates for protective coatings solely on the basis of melting point and static oxidation resistance. At the present time there is an increasing realization that the protection of the refractory metals from oxidation is a primary materials problem. Consequently increasing attention is being given to the design of coating systems and the criteria to be used in selecting materials for the coatings.

Some of the properties being considered in selecting potential coating materials are: oxidation resistance in static and rapidly flowing air and under thermal cycling conditions, thermal-expansion characteristics, elastic modulus, thermal conductivity, tensile or fracture strength, stability toward chemical reaction and interdiffusion with the substrate, thermal-shock resistance, and gaseous transport characteristics. Other properties of interest in selecting materials for coatings, especially for space applications, are emittance and material stability to ultrahigh vacuums and to electromagnetic and particulate radiations.

Previously cited references on materials contain excellent compilations of data on several of these properties. Experimental methods for property determinations at the high temperatures of interest are reviewed in References 28, 63, and 123, which also contain much information on materials. Reviews of mechanical-property data, particularly with respect to brittle materials, are given in References 3, 28, 29, 31, 32, 39, 124, 125, and 262.

Thermal Expansion

Close matching of the thermal-expansion characteristics of a coating with those of the substrate to be protected is considered to be a highly desirable feature for a successful coating system. The numerous reference. given previously for the various materials discussed contain many thermal-expansion data.

The Lawrence Radiation Laboratory has been compiling thermal-expansion data for pure dense materials melting above 1000 C. A preliminary tabulation of these data, as reported by Kr- orian[126], is presented in Table 10.

A comprehensive investigation of the theoretical and practical aspects of the thermal expansion of ceramic materials has been in progress at the Cornell Aeronautical Laboratory. The literature was surveyed during the first phase of this program, and data and references were compiled on the reversible thermal expansion of crystalline ceramics, rocks and minerals, glasses, cermets, intermetallic compounds, salts, cements, glazes, enamels, and ceramics, combined with other types of materials.[137] Several investigators have noted that crystals having rather "open" structures tend to have low thermal-expansion characteristics. With the aim of using this as a possible prediction method, openness ratios (the fraction of the lattice volume not occupied by ions) were calculated for about 1400 phases[128,129]. Subsequently, a comparison was made between the thermal expansion and openness ratio of approximately 200 pure phases, and it was found that a high openness ratio is not alone a sufficient criterion for the prediction of low thermal expansion.[130] Considerable additional research has been done in this program, and many thermal-expansion data have been generated.[131]

References 132 and 133 also present thermal-expansion data for several high-temperature materials of interest as protective coatings.

Thermal-Shock Resistance[28,32,53,63,117,119,134-140]

The term "thermal shock" designates a condition brought about by sudden and severe changes in the temperature at the surface of a solid body. These temperature changes produce transient temperature gradients which in turn cause various parts of the body to expand different amounts. Free expansion of each small unit of volume cannot take place, if the material remains intact, and thermal stresses result. When these stresses exceed the material strengths, fracture and disintegration of the material can result.

Ductile materials react in considerably different manners to thermal stress than do brittle materials. Brittle materials can undergo only a small amount of strain before rupture; whereas, ductile materials can undergo appreciable strain without rupture. Temperature gradients which can build up, and the resulting stresses in metallic materials are generally not so severe as in brittle nonmetallic materials.

The magnitude of thermal-shock stresses depends on the details of the thermal environment and the thermal and mechanical properties of the material. Thermal-shock resistance has been discussed in several reviews.[28,63,134,135] Kingery[63] has presented an excellent discussion of the subject and has compiled a list of important

TABLE 10. THERMAL EXPANSION OF HIGH-TEMPERATURE MATERIALS[126]

Material	Per Cent Expansion From 25 C (77 F) to Indicated Temperature				
	500 C (930 F)	1000 C (1330 F)	1500 C (2730 F)	2000 C (3630 F)	2500 C (4530 F)
Elements:					
Be	0.75	1.80			
B	0.39	0.81			
Nd	0.36	0.70 (800 C)			
Gd	0.32	0.97			
Tb	0.45	1.14			
Dy	0.49	1.20			
Er	0.50	1.25			
U (α)	0.85	1.27 (662 C)			
U (β)	1.57 (662 C)	1.77 (770 C)			
U (γ)	1.70 (770 C)	2.25			
Ti (α)	0.50	0.91 (882 C)			
Zr (α)	0.33	0.62 (870 C)			
Zr (β)	0.40 (870 C)	0.52	0.82 (1500 C)		
Hf	0.28	0.58			
Th (α)	0.60	1.22	1.72 (1400 C)		
Th (β)		1.69 (1400 C)			
V	0.46	1.04			
Cb	0.38	0.81	1.28	1.78	
Ta	0.31	0.69	1.10	1.59	2.05
Cr	0.42	1.07	2.02	2.18 (1800 C)	
Mo	0.28	0.56	0.96	1.47	1.98
W	0.215	0.465	0.75	1.07	1.45
Mn (α)	1.70	2.53 (727 C)			
Mn (β)	3.83 (727 C)	4.94	5.34 (1101 C)		
Mn (γ)		5.66 (1101 C)	5.81 (1137 C)		
Mn (δ)		6.17 (1137 C)	6.61 (1244 C)		
Re	0.32	0.67	1.04	1.44	
Fe (α)	0.68	1.32 (900 C)			
Fe (γ)	0.96 (900 C)	1.17	2.09 (1390 C)		
Fe (δ)		2.27 (1390 C)	2.54		
Ru	0.37	0.46 (600 C)			
Os	0.26	0.32 (600 C)			
Co (β)	0.63	1.80			
Rh	0.45	1.05	1.79		
Ir	0.34	0.77	1.27	1.80	
Ni	0.75	1.67			
Pd	0.61	1.36			
Pt	0.46	1.02	1.67	2.04 (1770 C)	
Cu	0.88	2.10	2.35 (1083 C)		
Au	0.73	1.65	1.80 (1063 C)		
C (diamond)	0.122	0.344	0.647		
Si	0.168	0.383			
Borides:					
SiB$_6$	0.25	0.58			
CaB$_6$	0.24	0.57			
BaB$_6$	0.28	0.63			
LaB$_6$	0.23	0.56			
CeB$_6$	0.30	0.65			
SmB$_6$	0.28	0.63			
ZrB$_2$	0.27	0.64	1.03		
HfB$_2$	0.25	0.54			

TABLE 10. (Continued)

| Material | Per Cent Expansion From 25 C (77 F) to Indicated Temperature | | | | |
	500 C (930 F)	1000 C (1830 F)	1500 C (27.0 F)	2000 C (3630)	2500 C (4530 F)
Carbides:					
Be_2C	0.48				
B_4C	0.23	0.54	0.89	1.29	1.75
SiC	0.22	0.50	0.81	1.14	1.47
TiC	0.34	0.75	1.20	1.74	2.40
ZrC	0.29	0.64	1.04	1.51	
HfC	0.30	0.61			
CbC	0.31	0.69	1.10		
TaC	0.30	0.65	1.05	1.51	2.08
Cr_3C_2	0.38	0.97			
Mo_2C (β)	0.26	0.60			
W_2C	0.17	0.37	0.59	0.84	1.17
WC	0.21	0.48	0.79	1.15	
UC	0.44	1.04	1.74	2.58	
U_2C_3	0.36	0.89	1.58	2.02 (1800 C)	
UC_2	0.30	0.92	1.86	2.60 (1800 C)	
Silicides:					
Cr_3Si	0.47	1.08			
$CrSi_2$	0.57	0.87 (700 C)			
Mo_3Si	0.27	0.68			
$MoSi_2$	0.37	0.83			
WSi_2	0.37	0.81			
Nitrides:					
BN	0.58	1.30			
AlN	0.23	0.54			
Si_3N_4 (α)	0.10	0.28	0.54		
Si_3N_4 (β)	0.07	0.22	0.46		
UN	0.38	0.84			
Oxides:					
BeO	0.36	0.88	1.52	2.19	
MgO	0.61	1.33	2.23	2.82 (1800 C)	
CaO	0.56	1.28	2.25		
SrO	0.59	1.32	1.64 (1200 C)		
TiO	0.43	1.20			
FeO_{1-x}	0.56	1.42			
ZnO	0.28	0.66	0.82 (1200 C)		
SiO_2 (α-quartz)	0.92	1.22 (575 C)			
SiO_2 (β-quartz)	1.53 (575 C)	1.42			
SiO_2 (α-trid.)	0.17 (117 C)				
SiO_2 (β_1-trid.)	0.23 (117 C)	0.38 (163 C)			
SiO_2 (β_2-trid.)	0.44 (163 C)	0.92 (500 C)	1.02 (1000 C)		
SiO_2 (vitreous)	0.025	0.055			
TiO_2	0.39	0.86	1.40		
ZrO_2 (monocl.)	0.31	0.74	0.79 (1050 C)		
ZrO_2 (tetr.)		- 2.23 (1050 C)	- 1.64	- 1.50 (1600 C)	

TABLE 10. (Continued)

| Material | Per Cent Expansion From 25 C (77 F) to Indicated Temperature | | | | |
	500 C (930 F)	1000 C (1930 F)	1500 C (2730 F)	2000 C (3630 F)	2500 C (4530 F)
HfO_2 (monocl.)	0.26	0.57	0.93	1.08 (1700 C)	
HfO_2 (tetr.)			0.22 (1700 C)	0.60	
CeO_2	0.39	0.87			
ThO_2	0.41	0.92	1.50	1.75 (1700 C)	
UO_2	0.45	1.09	1.43 (1200 C)		
SnO_2	0.16	0.41			
Al_2O_3	0.36	0.83	1.37		
Sm_2O_3 (B form)	0.43	1.02			
Eu_2O_3 (B form)	0.45	1.08			
Gd_2O_3 (C form)	0.43	1.02			
Dy_2O_3 (C form)	0.36	0.95			
Cr_2O_3	0.40	0.84	1.30		
Fe_2O_3 (α)	0.54	1.20			
Co_2O_3	0.55	0.72 (635 C)			
Cd_2O_3	0.44	1.02			
WO_3 (monocl.)	0.42 (330 C)				
WO_3 (orthorh.)	0.42 (330 C)	0.58 (500 C)	0.86 (730 C)		
WO_3 (tetr.)	0.81 (730 C)	1.32			
$MgAl_2O_4$	0.37	0.82	1.35		
$MnAl_2O_4$	0.31	0.70			
$FeAl_2O_4$	0.38	0.84			
$CoAl_2O_4$	0.36	0.83			
$NiAl_2O_4$	0.37	0.82			
$ZnAl_2O_4$	0.38	0.85	1.05 (1200 C)		
$MgCr_2O_4$	0.34	0.77			
$MnCr_2O_4$	0.41	0.91			
$FeCr_2O_4$	0.39	0.87	1.10 (1200 C)		
$ZnCr_2O_4$	0.39	0.85	0.96 (1200 C)		
$MgFe_2O_4$	0.49	1.18			
$ZnFe_2O_4$	0.43	0.96			
$Li_2O \cdot 5Al_2O_3$	0.34	0.81			
$Li_2O \cdot Al_2O_3$	0.55	1.21			
$BeO \cdot Al_2O_3$	0.35	0.78			
$3CaO \cdot 5Al_2O_3$	(0.09)	(0.22)	0.49 (1200 C)		
$BaO \cdot Al_2O_3$	0.32	0.73			
$2B_2O_3 \cdot 9Al_2O_3$	0.18	0.41			
$2CeO_2 \cdot 3Al_2O_3$	0.42	0.93			
$2ThO_2 \cdot 3Al_2O_3$	0.37	0.83			
$Co_2O_3 \cdot Al_2O_3$	0.37	0.83			
$2SnO_2 \cdot 3Al_2O_3$	0.34	0.75			
$BeO \cdot Cr_2O_3$	0.32	0.73			
$2BeO \cdot SiO_2$	0.27	0.62			
$2MgO \cdot SiO_2$	0.49	1.14			
$2CaO \cdot SiO_2$ (β)	0.63	1.40			
$MgO \cdot SiO_2$	0.50	1.05	1.60		
$CaO \cdot SiO_2$ (α)	0.47	1.09			
$CaO \cdot SiO_2$ (β)	0.27	0.40 (700 C)			
$2FeO \cdot SiO_2$	0.45	0.97			
$2ZnO \cdot SiO_2$	0.14	0.31			
$3Al_2O_3 \cdot 2SiO_2$	0.22	0.50	0.83		
$ZrO_2 \cdot SiO_2$	0.18	0.45	0.78		
$HfO_2 \cdot SiO_2$	0.14	0.32	0.44 (1300 C)		

TABLE 10. (Continued)

Material	Per Cent Expansion From 25 C (77 F) to Indicated Temperature				
	500 C (930 F)	1000 C (1830 F)	1500 C (2730 F)	2000 C (3630 F)	2500 C (4530 F)
$2MgO \cdot TiO_2$	0.48	1.07			
$MgO \cdot TiO_2$	0.34	0.77			
$MgO \cdot 2TiO_2$	0.39	0.86			
$CaO \cdot TiO_2$	0.62	1.37			
$SrO \cdot TiO_2$	0.41	0.92			
$Al_2O_3 \cdot TiO_2$	0.41	0.93			
$ZrO_2 \cdot TiO_2$	0.35	0.77	1.03 (1200 C)		
$MgO \cdot ZrO_2$	0.49	1.17	1.98		
$CaO \cdot ZrO_2$	0.43	1.02	1.31 (1200 C)		
$SrO \cdot ZrO_2$	0.42	0.94			
$BaO \cdot ZrO_2$	0.31	0.83			
$Cr_2O_3 \cdot ZrO_2$	0.23	0.55			
$CaO \cdot HfO_2$	0.29	0.71			

references. The theoretical approach to thermal-shock resistance is complex, and analytical solutions to the problem have been found only for simple geometries.

In general, the maximum temperature difference, ΔT_{max}, to which a body can be subjected before cracking or fracturing occurs is proportional to $R = \frac{\sigma}{E\alpha}$ and/or $R' = \frac{k\sigma}{E\alpha} = kR$, where R and R' are called the first and second thermal-stress-resistance factors, respectively, σ is fracture strength, E = modulus of elasticity, α = linear-thermal-expansion coefficient, and k = thermal conductivity. In some situations, ΔT_{max} may be inversely proportional to the thickness of the material. Therefore, from the standpoint of thermal-shock resistance, materials should be chosen on the basis of maximum strength and thermal conductivity, and minimum modulus of elasticity, thermal expansion coefficient, and thickness. Buessem[28] and Kingery[63] have compiled values of R and R' for various high-temperature materials. It has been found experimentally that the thermal-shock-resistance factors have reasonably good validity for the ranking of materials in order of merit.

Lauchner and Bennett[137], from their studies of cobalt-bearing ground-coat type of ceramic coatings on iron, concluded:

(1) Thermal-shock resistance is inversely related to the thermal-expansion characteristics of the coating.

(2) Increased thermal-shock resistance is gained by decreased coating thickness

(3) Residual compressive stress in a coating is a major factor in improved thermal-shock resistance.

Emittance

The temperature which a protective coating itself must withstand, and consequently the temperature at which the substrate must be protected from oxidation, depends, in many anticipated applications, on the aerodynamic-heat input and the emittance of the coated system. Therefore, the emittance of the system during operation in an oxidizing environment can be an important consideration.

Many emittance data, and other thermal-property data, available through 1957 have been reported by the Armour Research Foundation[34]. Due to the increased and particular interest in radiant-heat transfer and thermal-radiation properties of materials, the Defense Metals Information Center has been preparing a series of memoranda in the general field of radiant-heat transfer, with each memorandum being directed toward a particular area of interest.[141-146,176]

The rate of radiation from nonblackbodies, and therefore the emittance, depends upon the material, surface condition, and temperature. It has been found that emittance values for coating systems reported by one investigator may vary considerably from those for the same coating material and even the same coating system reported by another. The main reasons for such variances, assuming reasonable care in obtaining data, are differences in the surface condition, thickness of the coating, and substrate. Differences in surface condition result from differences in the methods of coating

application to the substrate and from numerous methods of bonding, curing, and finishing.

An innate property of most ceramic materials is their varying degree of transparency to radiation at different temperatures and different wavelengths. Because most protective coatings are kept as thin as possible due to considerations of weight, expansion mismatch, and thermal-shock resistance, the emittance of the substrate may, and usually does, have considerable effect on the measured emittance of the coating system.[145]

Another factor is that most of the currently promising coating systems have a continuously changing chemistry when in service due to controlled oxidation and interdiffusion.

Materials employed in space vehicles may be exposed to pressures of less than 10^{-10} mm Hg at a wide variety of temperatures. Under these conditions, especially for extended periods of time, evaporation could occur, resulting in a roughening of the surface as a consequence of the variation in free energy for various crystal planes. Surface roughening would be expected to alter the emittance.[147]

Therefore, emittance data for bulk materials considered as candidates for protective coatings can be translated to coating systems in service only with a good deal of reservation.

Stability Toward Radiation[147,148]

Although stability of thin materials to various kinds of radiation generally has not been considered in selecting oxidation-resistance coating materials, deleterious effects may be produced in a coating system of a space vehicle by radiation existing in space or possibly from a nuclear reactor.

Some inorganic solids are susceptible to damage by ultraviolet radiation. For example alkali halides, quartz, glass, and MgO are subject to discoloration. The formation of color centers by radiation can result in increased brittleness and hardness. Changes in density and thermal conductivity may also occur.

Loss of coating material might also occur by sputtering caused by impact with solar-wind ions and neutral atoms.

Modification of Materials to Achieve Desired Properties

It is probably not possible to obtain all of the properties desired in a protective coating on a particular substrate for a specific mission from a single compound. Therefore, modification of materials by forming mixtures and solid solutions and the use of duplexed materials appears to be very much in order. Some work has been and is being done along this line; much more will be required before major problems associated with protection of the refractory metals from oxidation can be considered solved.

Obviously, the oxidation resistance of the material, per se, desired for a coating is of prime importance. The effect of making major and minor additions to existing promising coating-material bases needs further research. The long history of the development of nonrefractory oxidation-resistant alloys shows that, in some cases, very small additions can make major changes in the oxidation resistance. (25,26,149,150) For example, Pfeiffer(150) reported that 0.2 per cent cerium increased the cyclic oxidation life of an Fe-27Cr-5Al alloy at 2200 F from 30 to 150 hours; 0.005 per cent calcium in this alloy increased the cyclic life to 300 hours. The addition of fluxing agents to silicide-base materials to aid in forming a protective oxide layer has been found to have merit. Sound detailed research to explore and extend these concepts in the area of coating materials for the refractory metals might be of much benefit.

Incorporation of a material into a coating base or duplexing of a material which would have or would oxidize to give a high emittance and increased erosion, impact, and thermal-shock resistance may be a possibility. Adjustment of thermal expansion and thermal conductivity would be of considerable value. And quite clearly, modifications of materials to increase ductility would lessen the severity of several problems encountered in coating systems.

A universally desired, vitally needed, but rarely achieved property of a coating material is the ability to tolerate defects. Although integrity is sought in any coating system, defects in the coating inevitably result from failures in application or cracking during service. The coating material or its reaction products with air and/or the substrate, therefore, should have the ability to tolerate a defect; this frequently is referred to as a self-healing quality. If a coating system had good defect tolerance, the coating-preparation process would be less critical and could be operated with greater flexibility. Also, thermal-expansion mismatch problems would be decreased, the coating would be less susceptible to damage during handling and assembly of hardware, and desirable mechanical, impact, erosion, thermal-shock, and thermal-cycling characteristics could be more easily achieved.

COMPATIBILITY

Chemical and Diffusional Compatibility of Coating Materials and Substrates

Selection of materials for coatings should always be made with reference to the substrate to be protected and the mission to be accomplished. Although this is an important rule to be borne in mind throughout the multiple avenues of research and development work on protective coatings, it is of utmost importance when chemical and diffusional compatibility of coating materials and substrates are considered.

Generally speaking, the higher the temperature, the greater the potential is for different materials to react and interdiffuse; and the higher the temperature and the longer the time, the greater is the extent to which reaction and diffusion occur. Chemical reaction and interdiffusion between coating and substrate can substantially reduce the thickness of the substrate, alter the mechanical properties on which the design of the structure was based, produce undesirable interface phases, and destroy the protective characteristics of the coating by changing the composition and the various properties originally designed into the coating.

What actually occurs in a coating system under a given set of time-temperature-pressure conditions depends on the thermodynamics of the system (where is the system headed) and the kinetics (how fast can the system proceed). Thermodynamics frequently is of help in determining the direction in which a system has the potential to go; however, lack of reliable thermodynamic data and insufficient knowledge regarding solubility limits and intermediate phases at the high temperatures of interest for coating systems often preclude the making of reliable predictions. Kinetic theory has not evolved to the point where good predictions can be made for interaction rates between the materials of interest in coating systems and at the temperatures of concern. Consequently, "rules of thumb" and the experimental approach are usually heavily relied upon.[25,153]

Chemical Reaction

Extensive compilations of thermodynamic data have been presented in readily available sources (References 6, 25, 28, 68-80, and 123). Compilations of pertinent phase diagrams are given in References 54, 90, 151, and 152. General thermodynamic stability relationships of refractory oxides are shown in Figure 10; and Table 11 gives values for the heats of formation of metal silicides, as compiled by Searcy[92].

At sufficiently high temperatures, all refractory metals will react with oxide materials. This is particularly true in vacuo where many vapor species containing reduced oxygen content are formed, as pointed out by Kingery[29]. Some reaction temperatures between refractory oxides and tungsten and molybdenum involving gross changes observed by Johnson[154] are given in Table 12.

TABLE 11. HEATS OF FORMATION OF METAL SILICIDES[92]

Silicide	Negative of Heat of Formation, kcal/g-atom of silicon	Silicide	Negative of Heat of Formation, kcal/g-atom of silicon
$ZrSi_{0.25 \pm 0.05}$	52 ± 6	$CbSi_{0.55 \pm 0.05}$	21 ± 10
Zr_2Si	50 ± 6	Cb_5Si_3 (tetr.)	21 ± 10
Zr_5Si_3	46 ± 4	Mo_3Si	21 ± 5
Zr_3Si_2	46 ± 6	$ThSi_2$	21 ± 5
Ti_5Si_3	46 ± 3	$ZrSi_2$	19 ± 4
$ZrSi_{0.83 \pm 0.05}$	41 ± 4	$CeSi_x$	<17
$ZrSi$	37 ± 4	$TiSi_2$	$16 \pm$
V_2Si	37 ± 5	W_5Si_3 (tetr.)	1
$TaSi_{0.22 \pm 0.05}$	32 ± 4	$CbSi_2$	
Ta_2Si	31 ± 4	$MoSi_2$	
$TiSi$	31 ± 4	$TaSi_2$	13 ± 3
Ta_5Si_3 (tetr.)	29 ± 4	$ReSi_{0.5 \pm 0.1}$	13 ± 4
$CeSi_2$	25 ± 10	$ReSi$	10 ± 4
$MoSi_{0.65 \pm 0.05}$	22 ± 3	$ReSi_2$	8 ± 4
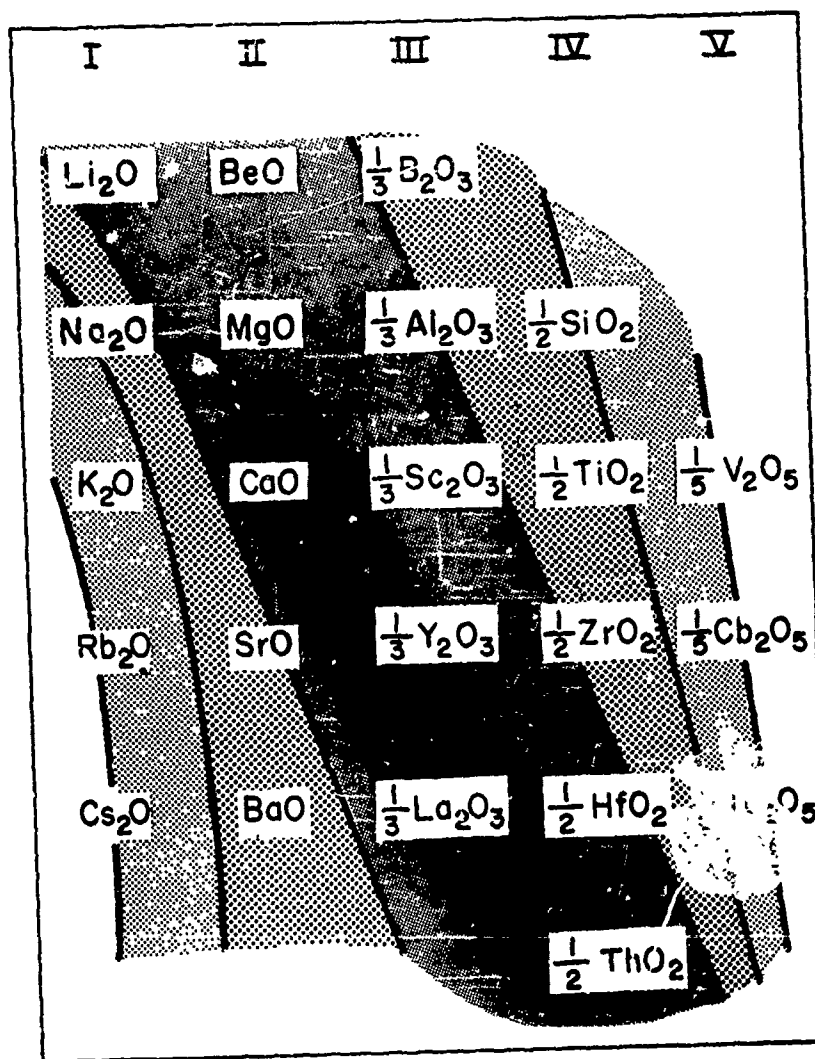
FIGURE 10. STABILITY RELATIONSHIPS OF REFRACTORY OXIDES

Solid lines are lines of constant standard free energy of
formation from the elements. The darkly shadowed area
is the region of greatest stability.

[Kingery[29]]

TABLE 12. REACTION TEMPERATURES (C) FOR REFRACTORY
COMBINATIONS IN VACUO[154]

	W	Mo	Al_2O_3	BeO	MgO	SiO_2	ThO_2	ZrO_2
W	--	2300	>2000	2100	2000	1600	2300	2100
Mo	2300	--	2000	1900	1800	1500	2200	2150

Information on reaction between several oxides and metals, as reported by
Economos[155], is given in Table 13. For these experiments the oxides and metals were
fabricated into disks, polished, and then assembled into a reaction couple by placing the
metals on top of the oxides. The desired temperature was attained by heating above
300 C (570 F) at the rate of 20 C (36 F) per minute until the temperature was reached.
This temperature was held for 15 minutes in the helium atmosphere.

Reactions between tungsten and Al_2O_3 at temperatures between about 2700 and
3600 F have been under investigation recently in studies of heater-cathode breakdown
phenomena.[156,157]

Resnick and Steinitz[177] recently reported that, in general, the combination of
tungsten and refractory oxides, MgO excepted, are inert at temperatures exceeding t
melting points of the oxides. Combinations of tungsten and various carbides and nitric
were reported as being quite reactive at temperatures well below 5400 F. Experimental
results from this work are presented in Table 14.

Bergeron, Tennery, and Friedberg[158] studied zircon-glass coated tungsten in
air at 3000 F for times up to 10 hours. They attributed the formation of tungsten oxides
to gradual migration of oxygen through the coating to the tungsten substrate.

Diffusion

Intimately associated with chemical reaction phenomena is the subject of solid-
state diffusion which provides the mechanism for reaction to occur.[153,159]

Peterson[159] recently reviewed and evaluated data in the open literature on
diffusion in tungsten, tantalum, molybdenum, columbium, hafnium, zirconium, vanadium,
chromium, and titanium. Information was compiled on 95 binary systems and 13 ternary
or higher-order systems. Subsequent work on this program has as its goal the determi-
nation of the interdiffusion coefficients, as functions of composition and temperature, of
the systems W-Rh, W-Pt, W-Ir, and W-Ru.[160]

Barriers to be used between protective coatings and refractory-metal substrates
are being investigated by Passmore et al.[161,162] If the dissolution of the coating or the
formation of undesirable constituents by interdiffusion can be prevented by use of a
barrier, it is thought that the problem of finding suitable oxidation-resistant coatings
may be made easier.

TABLE 13. SUMMARY CHART(a, b) OF REACTION BETWEEN OXIDES AND METALS

Mo

Compound	Temperature, C 1400	1600	1800	New Products
Al₂O₃	NR	NR	NR	--
BeO	•	NR	NR	--
MgO	NR	NR	NR	--
ThO₂	•	NR	✶	--
TiO₂	NR	NR	NR	--
ZrO₂	NR	NR	NR	--

Ni

Compound	Temperature, C 1400	1600(c)	1800	New Products
Al₂O₃	NR	NR(c)	NR	--
BeO	•	NR	•	--
MgO	NR	NR	NR	--
ThO₂	•	NR	✶	--
TiO₂	NR	NR	NR	--
ZrO₂	NR	NR	NR	--

Cb

Compound	Temperature, C 1400	1600	1800	New Products
Al₂O₃	NR	NR	NR	Cb₂O₅
BeO	•	SR	VR	Cb₂O₅
MgO	NR	SR	SR	Cb₂O₅
ThO₂	•	NR	✶	--
TiO₂	NR	SR	VR	--
ZrO₂	SR	SR	VR	--

Ti

Compound	Temperature, C 1400	1600	1800	New Products
Al₂O₃	NR	SR	VR	TiO₂
BeO	•	SR	VR	TiO₂
MgO	SR	SR	VR	MgO·TiO₂
ThO₂	•	NR	NR	TiO₂
TiO₂	NR	SR	✶	?
ZrO₂	NR	SR	VR	TiO₂ s.s. of Ti

Be

Compound	Temperature, C 1400	1600	1800	New Products
Al₂O₃	NR	NR	SR	BeO·Al₂O₃
BeO	S?	SR	•	--
MgO	SP	VR	O	BeO
ThO₂	SP	SR	✶	?
TiO₂	NR	VR	O	--
ZrO₂	NR	SR	O	BeO

Si

Compound	Temperature, C 1400	1600	1800	New Products
Al₂O₃	SR	VR	O	SiO₂: 3Al₂O₃·2SiO₂
BeO	•	VR	•	--
MgO	SR	VR	O	2MgO·SiO₂
ThO₂	•	VR	•	--
TiO₂	SR	VR	O	SiO₂
ZrO₂	NR	VR	O	ZrO₂·SiO₂

Zr

Compound	Temperature, C 1400	1600	1800	New Products
Al₂O₃	NR	SR	VR	ZrO₂
BeO	•	SR	VR	ZrO₂ (*)
MgO	NR	NR	SR	ZrO₂
ThO₂	•	NR	NR	ZrO₂
TiO₂	NR	SR	✶	?
ZrO₂	NR	NR	SR	--

(a) Compiled by Economos(155).

(b) Code: NR = no perceptible reaction. SR = slight reaction as shown by surface discoloration and penetration; VR = violent reaction as shown by presence of a new phase or surface corrosion. O = omitted because of excessive volatilization of the metal. at 1800 C: ✶ = omitted because TiO₂ fused below 1800 C. • = omitted because only few specimens were available (strategic materials). ? = X-ray lines show unidentified reaction products. s.s. = solid solution shown by d-line shift in X-ray study.

(c) Underscoring indicates molten metal in contact with the oxide

TABLE 14. RESULTS OF REACTIONS BETWEEN TUNGSTEN FOILS AND REFRACTORY COMPOUNDS

System	Temperature, F	Time, minutes	Metallographic Observations	Phases Detected by X-ray Analyses
$W + ThO_2$	5070	1	Particles sintered to foil. No other reaction.	W, ThO_2
	5430	1	Ditto	
	5430	3	Ditto	
$W + ZrO_2$	4530	1	Particles sintered to foil. No other reaction.	
	5070	1	ZrO_2 partially molten. Adhered to the foil. No evidence of other reaction	W, ZrO_2 lines prominent
	5430	1	ZrO_2 completely molten. Adhered well to the foil. No indication of other reaction.	
$W + MgO$	4000	1	Some slight sintering. Interface slightly irregular.	W
	4530	5	Interface severely eroded. All of the MgO reacted.	
	5430	1	Same as above.	
$W + Al_2O_3$	4000	1	Al_2O_3 molten. No reaction. Oxide did not adhere to the foil.	W, Al_2O_3
	4530	5	Al_2O_3 molten. Wet and adhered to foil. Interface is very sharp. No reaction.	
	5430	1	Same as above. Al_2O_3 vaporizing fairly rapidly.	
$W + Y_2O_3$	4000	2	Particles sintered to foil. No other reaction.	W, Y_2O_3
	4530	1	Y_2O_3 molten. No other reaction.	
	5430		Y_2O_3 molten. No other reaction.	
$W + HfO_2$	5240	2	HfO_2 molten, wets tungsten. Slight reaction in the form of interdiffusion. No new phases distinguishable.	W, HfO_2
	5430	1	Same as above.	
$W + TiN$	5070	1	No significant reaction.	W, TiN
	5240	2	TiN molten. Slight reaction at the interface.	
$W + ZrN$	5070	1	Interface is slightly irregular. ZrN sinters to the W.	$W + ZrN + W_2Zr$
	5240	2	About the same as above.	
	5430	1	Severe irregularities at the interface. A metallic like phase is dispersed in the ZrN. New phase also appears at the interface.	
$W + TaC$	4880	1	Sintering of TaC to tungsten foil.	W, TaC and $(W, Ta)_2C$
	4880	2	Similar to above.	
	5160	1	Eutectic composition forms and melts.	
$W + HfC$	2800	2	A eutectic forms which melts at about this temperature.	W, HfC and b.c.c. Hf
$W + ZrC$	4890	1	A eutectic forms which melts below 4890.	W, ZrC

TABLE 14. (Continued)

System	Temperature, F	Time, minutes	Metallographic Observations	Phases Detected by X-ray Analyses
W + (80%Ta, 20%Hf)C	4890	1	A eutectic forms which melts below 4890.	W, ZrC
	5070	2	Diffusion layer much thicker than above. Considerable erosion of the tungsten is evident.	(Ta, Hf)C, W
	5070	2	About the same as 5070 specimen.	

During the first year of work on this program[161], 23 substrate-barrier combinations were screened by studying the interdiffusion which occurred by annealing at 1700 C (3010 F). It was concluded that hafnium and iridium were the most promising barriers for tungsten at this temperature, with vanadium as a third choice. Iridium appeared to be the best choice for tantalum and molybdenum. No recommendation could be made for columbium, primarily because of melting at the screening temperature. A comparison of interdiffusion behavior with substrate-barrier phase relations indicated no correlation with either solid solubility or presence of intermediate phases. The melting points of both barrier and substrate appeared to be the most important factors affecting the extent of interdiffusion.

As a result of the findings during the first year of this program on diffusion barriers, the following couples, which were excluded from investigation initially because of extensive solid solubility, were scheduled for study[162]: W-Cr, Ta-Re, Ta-V, Mo-Re, Mo-V, Mo-Pt, Cb-Re, Cb-Ru, Cb-Hf, Cb-V, and Cb-Zr. Also, the major refractory metals themselves were scheduled for investigation for possible use as barriers for each other. This work is currently in progress.

Birks and Seebold studied the diffusion of columbium with stainless steels and their major constituents (chromium, iron, nickel, molybdenum) at about 1100 C (2010 F)[163] and diffusion of the following binaries, also at 1100 C: Cb-Pt, Cb-Se, Cb-Zn, Cb-Co, Ta-Ni, and Mo-Fe[164]. The objective of this work was to obtain information which possibly would aid in designing better cladding alloys to protect against oxidation. Intermetallics were formed in all of these systems as a result of interdiffusion at 1100 C, with the exception of the Cb-Mo system which has complete miscibility.

In general, the diffusion of Cb with the components of stainless steel (iron, nickel, chromium) led to hard, brittle phases and often to physical voids or cracking[163]. Cracking often occurred in the diffusion zone, usually between the intermediate phases or near the columbium-poor side of the zone but never near the columbium-rich side. It was judged that poor physical compatibility as a result of intermediate-phase formation could be the cause of cracking that often occurs in stainless-clad columbium. At 1200 C (2190 F) the diffusion in the Cb-Cr couple was so rapid that columbium diffused throughout the original 5-mil chromium layer in 24 hours. Cb-Ni couples often melted near 1100 C (2010 F), approximately 75 C below the reported eutectic temperature. Table 15 gives the phases identified as having formed in various binary diffusion couples at 1100 C (2010 F).

Fugardi and Zambrow[165] investigated materials for diffusion barriers between Type 310 stainless steel and columbium or molybdenum sheet. The best barrier material found, on the basis of tensile strength, thermal-shock resistance, minimum diffusion during long time at 1000 C (1830 F), and minimum formation of intermetallics at the bonding surfaces, was nickel for molybdenum and iron for columbium. Diffusion-zone thicknesses produced at 1000 C for various combinations are given in Table 16.

Growth of the diffusion zone between molybdenum and chromium, nickel, and cobalt with time and temperature is shown in Figures 11 and 12. Interdiffusion of nickel-base materials with molybdenum has been observed as a problem in using coatings of this nature.[41,43] Levinstein[43] reported that all nickel-base (and boron containing) coatings investigated at General Electric for turbine buckets reacted with the molybdenum substrate when heated to elevated temperatures (1800 to 2000 F) to form an intermetallic

TABLE 15. PHASES FORMED DURING BINARY DIFFUSION AT
1100 C (2010 F)[163,164]

Diffusion Couple	Phases
Cb-Cr	$CbCr_2$, $CbCr_7$, CbC + Cb
-Fe	$CbFe_2$ + Fe
-Ni	$CbNi$ + Cb, Cb_2Ni, $CbNi_3$
-Pt	Cb_3Pt, $CbPt$, $CbPt_2$, $CbPt_3$
-Se	$CbSe$, Cb_2Se_3, $CbSe_2$
-Zn	$CbZn$, Cb_2Zn_3, $CbZn_2$, $CbZn_3$
-Co	Cb_3Co_2, $CbCo_4$
Ta-Ni	$TaNi_3$, $TaNi_2$, $TaNi$, Ta_3Ni_2
Mo-Fe	Mo_2Fe_3

TABLE 16. ZONE THICKNESS PRODUCED BY INTERDIFFUSION AT 1000 C (183? F)[165]

Diffusion Couple	Thickness of Diffusion Zone, inches x 10^4, After Indicated Time				
	1 Day	2 Days	3 Days	4 Days	10 Days
Fe-Mo	3.672	14.920(a)	(b)	--	--
Ni-Mo	1.976	3.560	--	--	7.5000
Ti-Mo	4.790	8.790(a)	20.696(a)	--	--
Cu-Mo	0.319	1.590	(a)	--	(b)
Monel-Mo	4.434	--	6.490	--	--
Pd-Mo	1.296	12.900	25.016	--	--
Fe-SS	17.460	19.150	26.700	27.10	27.000
Ni-SS	16.650	24.210	38.920	--	40.000
Ti-SS	19.860	68.530	(b)	--	---
Cu-SS	3.240	4.320	6.060	--	--
Monel-SS	23.280	--	48.880	--	--
Pd-SS	8.426	9.102	14.692	--	--
Ta-SS	2.372	6.480	--	--	--
Fe-Cb	5.288	8.538	11.308	--	15.000
Ni-Cb	17.873	20.006	22.296	(b)	--
Ti-Cb	22.000	(b)	(b)	--	--
Cu-Cb	0.000	0.100	0.100	1.28	(b)
Monel-Nb	(b)	(b)	(a)	--	--
Pd-Cb	2.596	7.170	13.012	--	--

(a) Unbonded.
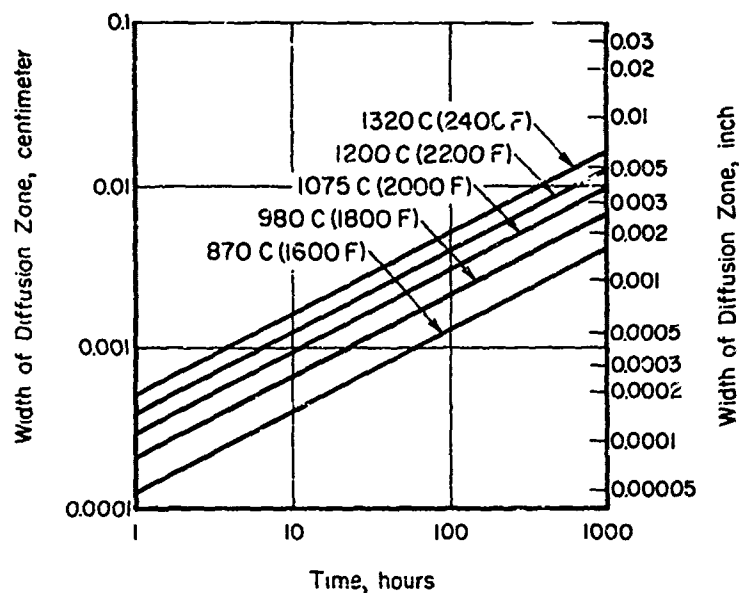(b) No zone measurements obtainable.

FIGURE 11.   VARIATION OF THE WIDTH OF THE MOLYBDENUM-CHROMIUM
DIFFUSION ZONE WITH TIME AT VARIOUS TEMPERATURES[166]
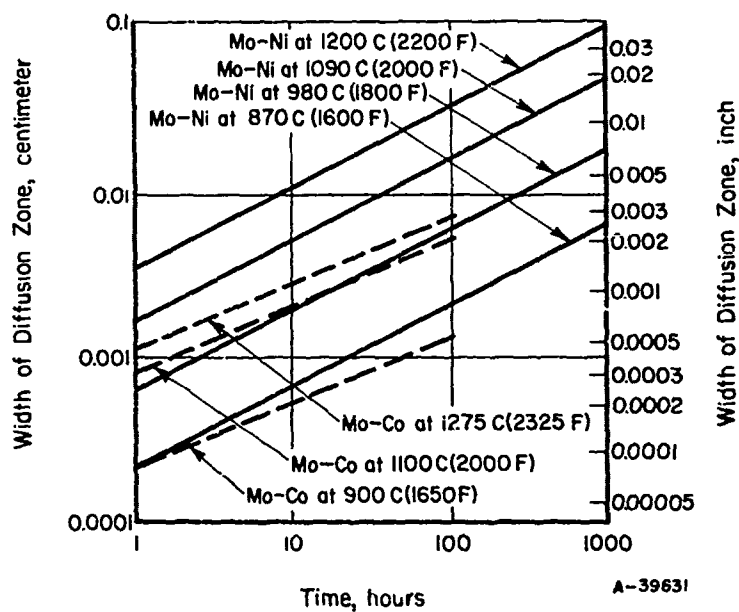

FIGURE 12.   VARIATION OF THE WIDTH OF THE MOLYBDENUM-NICKEL AND
MOLYBDENUM-COBALT DIFFUSION ZONES WITH TIME AT
VARIOUS TEMPERATURES[166]

layer wh..h initiated recrystallization in the molybdenum at the interface. Chromium, when used as a barrier between nickel and molybdenum, effectively retards inter-diffusion. Figure 13 shows the interdiffusion observed by Brenner et al.[245] in nickel-chromium plated molybdenum after 600 hours at 1100 C (2010 F). Safranek and Schaer[166] reported that a gold-chromium barrier reduced the interdiffusion between molybdenum and nickel-chromium.
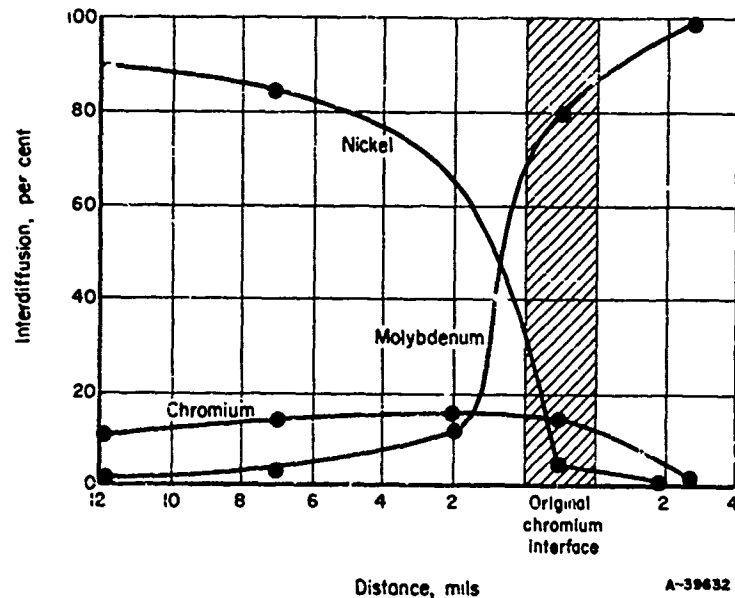
FIGURE 13. INTERDIFFUSION OF COMPONENTS OF A MOLYBDENUM BAR PLATED WITH NICKEL AND CHROMIUM AFTER 600 HOURS AT 1100 C[245]

Figure 14 shows the relatively rapid diffusion which was observed by Sama and Lawthers[210] for beryllide-coated tantalum and Ta-10W. It should be particularly noted that, after 15 hours at 2500 F, a 9-mil substrate of tantalum was reduced to about 2 mils by diffusion, whereas the Ta-10W substrate under the same conditions was reduced in thickness to only about 7 mils.

Although quantitative data are not available, all of the current popular and promising coatings prepared by diffusion processes are, by their very nature, subject to degradation during service via interdiffusion between the substrate and coating. The amount of degradation in all of these systems can be expected to increase with temperature and time.

Coating systems, particularly at the higher temperatures (~3000 F and higher),are sometimes evaluated by means of induction heating. Because induction heating has been reported as giving diffusion rates, during the coating of steel, several hundred times higher than those obtained by furnace heating[167], it would seem that this technique of
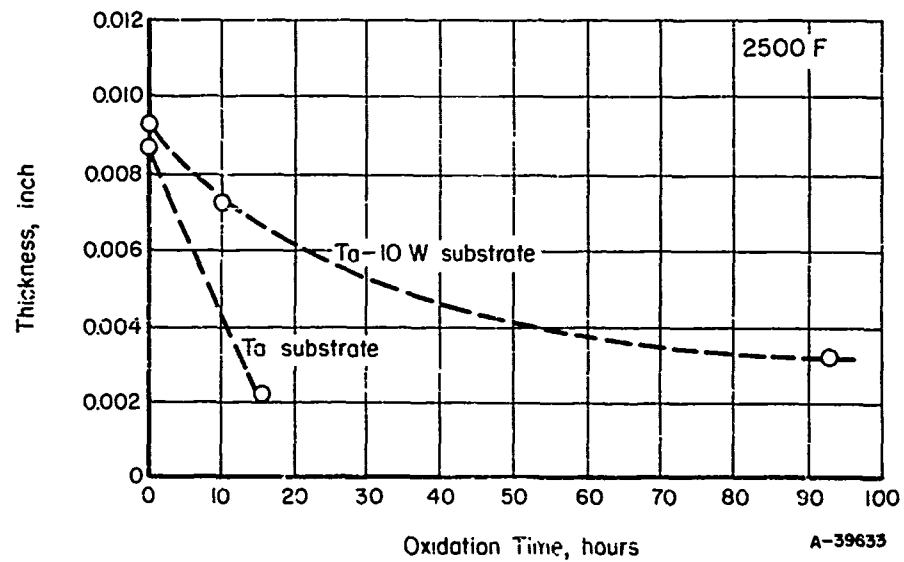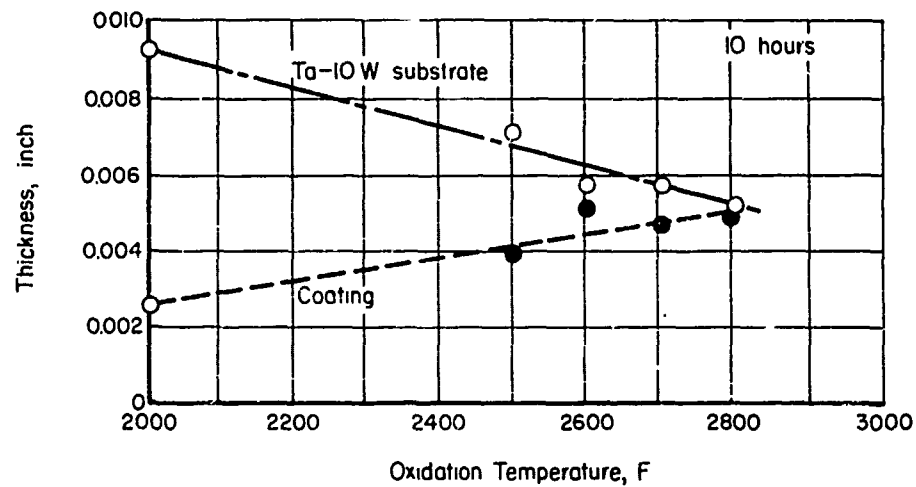
FIGURE 14. DIFFUSION EFFECTS AT VARIOUS TIMES AND TEMPERATURES
ON BERYLLIDE-COATED SAMPLES[210]

heating for evaluation should be used with reservation until it can be shown that inter-diffusion in refractory-metal systems is not being accelerated. Several schools of thought exist as to why induction heating can cause greatly accelerated diffusion; so far no uniform theory exists.

Structural Compatibility of Coating
Materials and Substrates

Structural or mechanical compatibility between a coating and a substrate is desirable in a coating system. Good compatibility consists of matching the properties of the coating and substrate so that they do not induce undesirable stresses in each other.

One aspect is the effect of the coating on fatigue life and brittle transition temperature of the coating system.[5] Because the coating generally will be more brittle than the substrate, the coating will be more susceptible to the formation of cracks which can act as stress risers on the substrate and reduce the low-temperature ductility and fatigue life.

A very significant degree of incompatibility can occur by thermal-expansion mismatch between the coating and the substrate, causing stresses which exceed the yield point of either of the materials. The result can be spalling or cracking of the coating, distortion of the composite, or failure of the bond.

There is a common misunderstanding that thermal-expansion matching and thermal-shock resistance refer to the same phenomenon, but in fact, they do not. Thermal shock involves transient thermal gradients, and, the lower the thermal-expansion coefficient of a material, the greater is its resistance to thermal shock because the lower are the stresses produced by the gradients. If the thermal-expansion characteristics of a coating are severely mismatched to those of the substrate, remarkably large and severely damaging stresses can be built up, even under isothermal conditions. The difference in the two phenomena brings out a mutually incompatible set of requirements for a coating system. For maximum thermal-shock resistance of the coating, the lowest possible thermal-expansion coefficient is desired. Yet, for maximum structural compatibility with the substrate, the thermal-expansion characteristics of the coating should match those of the substrate.

Figure 15 shows some theoretical stress relationships reported by Graham, Luft, and Sayre of the General Electric Co. where this aspect of protective-coatings technology has been under active investigation.[5,61,171] The last column shows that, under conditions of rapidly changing temperature, serious thermal stresses can occur regardless of how well or how poorly matched the thermal expansions of the coating and substrate are.

The thermal-expansion-match theory has not been widely used in studies of protective coatings for the refractory metals.[5] The electronics and ceramics industries have been able to overcome some fairly serious expansion-mismatch problems in making glass-to-metal and ceramic-to-metal seals by using specially designed alloys and graded seals.[168-170] Although the materials involved in these applications generally are not applicable to the high-temperature coatings problem, some of the principles involved should be.
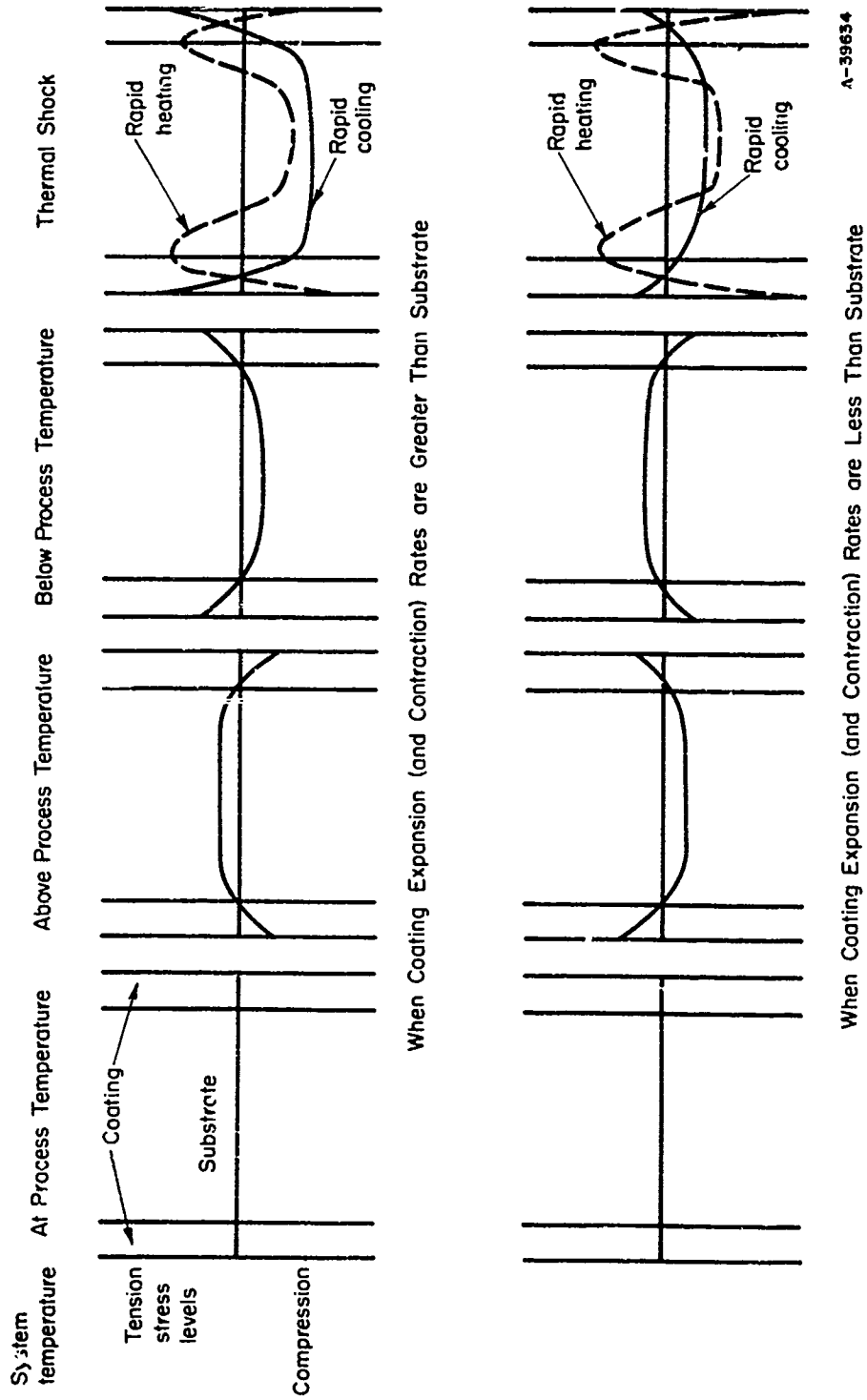
FIGURE 15. THEORETICAL STRESS RELATIONSHIPS IN A COATING SYSTEM[5]

Oxx[172] reported the following formula for estimating the stress induced in a coating by thermal change, from the temperature of zero stress, of a flat plate coated on both sides:

$$S_c = \frac{E_s E_c}{E_s + 2E_c \frac{t_c}{t_s}} \ \Delta T \ \Delta \alpha_{s,c} \ ,$$

where

S_c = coating stress
E_c, E_s = elastic moduli of coating and substrate
α_c, α_s = linear-thermal-expansion coefficients
t_c, t_s = thicknesses
ΔT = temperature change from temperature of zero stress.

As shown in Figure 15, the type of stress resulting from expansion mismatch depends on the relative expansion coefficients of the coating and substrate and the temperature relative to the temperature of zero stress, which is assumed in Figure 15 to be the temperature at which the coating is applied. Because virtually all stable coating systems are brittle at low temperatures, and because the compressive strength can be expected to be 5 to 10 times that of the tensile strength of these materials, if expansion mismatch must exist, it is advantageous to have the coating in compression.

Graham, Luft, and Sayre[5,171] correlated crack magnitude (the product of crack width and crack frequency) in brittle coatings on molybdenum and columbium with thermal-expansion mismatch. The higher the thermal-expansion coefficient of the coating relative to the substrate, the larger was the crack magnitude and the lower was the protective life of the coating.

Damage can result from expansion mismatch with ductile coatings also. Fugardi and Zambrow[165], in making butt welds on composite sheets of Type 310 stainless-molybdenum and Type 310 stainless-columbium, found that the difference in thermal expansion between the stainless and the refractory metals caused stresses and distortion in the weldments. Levinstein[43] observed thermal-fatigue cracking due to expansion mismatch as a predominant mode of failure in cycling molybdenum protected with a chromium-nickel-NiSiB-Nichrome coating hard-faced with CoCrWB.

Reid and Ogburn[174] reported that a major factor contributing to the deterioration of the bond between nickel and chromium when plated on molybdenum is the difference in the expansion coefficients of the three metals. An equation, used by Lander and Germer[175] to explain spalling, was applied to the problem of edge separation in this system:

$$S_n = \frac{2t_c}{d} \ (\alpha_B - \alpha_A) \ E_B \ \Delta T,$$

where

S_n = stress normal to the interface for a cylinder of metal A plated with metal B, neglecting plastic flow

t_c = coating thickness

d = diameter of the cylinder

α_B, α_A = linear-thermal-expansion coefficients

E = elastic modulus

ΔT = temperature change above room temperature.

If a molybdenum surface, with a radius of curvature of 0.3 inch, plated with 8 mils of nickel over 1 mil of chromium is heated to 800 C (1470 F), the calculated normal stress is 5200 psi at the Ni-Cr interface and 1000 psi at the Cr-Mo interface. The stress at the Ni-Cr interface is of the order of the Ni-Cr bond strength in the system, and separation would tend to occur. Also, according to the equation, the smaller the radius of curvature and the thicker the coating, the greater should be the potential for coating separation. These predictions have been found to be in qualitative agreement with experimental findings.

PREPARATION OF COATING SYSTEMS

Coating Application Techniques[41,42,115,178-180]

Numerous methods and combinations of methods have been used to produce coating systems. These can be roughly categorized as follows:

(1) Plating from a solution or liquid vehicle
        Electroplating
             Aqueous
             Fused salt
        Electrophoretic deposition

(2) Chemical-reaction deposition
        Vapor plating
        Pack cementation
        Exothermic reaction

(3) Hot spraying
        Flame spraying
        Detonation or flame plating
        Plasma spraying

(4) Other application techniques
        Vacuum metallizing
        Cladding
             Roll and forge bonding
             Gas-pressure bonding

        Hot Dipping

        Paint and sinter or diffuse
        Slip casting
        Hand troweling.

Processes employing several of these methods involve subsequent treatment steps such as hydrogen reduction, diffusion annealing, sintering and densification, and infiltration of interconnecting pores. Each of these techniques has advantages and disadvantages, depending on the coating material, the composition, size, and geometry of the component to be coated, and the end-use application. Frequently the successful use of these methods depends heavily on the know-how and experience of the people using them. Although general underlying principles of the methods are known, there remains much art in several of the methods.

The most widely used technique at the present time appears to be the pack-cementation method. However, all of the techniques continue to be investigated, and several of the other methods have been shown to have genuine merit for producing coating systems.

Plating From Solution or Liquid Vehicle

Electrodeposition techniques in general have advantages of relatively low temperatures of operation, ease of control of coating thickness. ability to coat complex shapes, facility for applying multilayered coatings, and the ability to coat finished parts. Disadvantages are the multiplicity of operations and complexity of procedures, the tendency to produce porous coatings, and the difficulty in obtaining adequate protection at the point of electrical contact.

Electroplating. Electroplating techniques have received much attention for applying coatings, particularly in former years when the major effort was concentrated on the protection of molybdenum at about 1800 to 2200 F. However, with the ever-increasing service-temperature requirements, there has been a decreasing interest in electroplating methods for producing coatings on refractory metals, because the metals and coating compositions for which methods have been worked out have relatively high diffusion rates at the temperatures of interest, and the melting points of the metals or interdiffusion products are relatively low. Also, other methods of producing coating systems have shown much promise.

General electroplating techniques for the refractory metals and results obtained have been reviewed by Beach and Gurklis[181], Safranek and Schaer[166], and Faust[115]. The extensive earlier work done on electroplating coatings on molybdenum was summarized by Bartlett, Ogden, and Jaffee[42]. Aluminum, brass, chromium, gold, iridium, palladium, platinum, and nickel are the most predominant metals that have been electroplated either singly or in complex layers for use in the protection of molybdenum from oxidation. Withers[183] recently investigated platinum and rhodium platings on molybdenum; stress cracks and pinholes in the coatings prevented protection at 2500 F for longer than 1 hour. In addition, many plating processes were investigated to produce an adherent preplate on columbium over which cermets could be plated; none was found to work well enough for the purpose. Hirakis[182] also investigated electroplated coatings on columbium. Early failure generally was experienced; this was believed to be due in part to blistering caused by entrapment of plating solutions, and in part to diffusion annealing required to obtain adhesion.

Goetzel, Venkatesan, and Bunshah[46] attempted to put an electroplated coating of rhodium on tungsten, but the protection obtained was only of limited value. The coatings were reported to be in a highly stressed condition, of a porous and crystalline nature, and they failed to inhibit passage of oxygen to the substrate. Introduction of intermediate layers of chromium, silicon, and chromium gave improved performance.

Kutzelnigg[191] recently reviewed the causes of porosity in electrodeposits, classified the various types of porosity, and discussed methods of assessing porosity.

Electrophoretic Deposition. [179,180,183-185,205,264] This is a process in which colloidal particles, suspended in a liquid medium, migrate in an electric field and deposit on an electrode. Migration occurs because the particles are electrically charged, either positively or negatively depending on the composition of the system. Lamb and Reid[184] have listed the following advantages for the method: (1) an electrophoretic coating is denser than one applied by dipping or spraying, (2) the thickness of the coating

can be closely controlled, (3) objects of irregular shape acquire a coating that is fairly uniform in thickness, because when points and edges have been covered, the insulating effect of the coating on these areas diverts the current to recessed areas, and (4) the rate of deposition is high because the depositing particles have a high ratio of mass to charge. (Under typical operating conditions, an electrophoretic deposit attains a thickness of 1 mil in about 10 seconds, whereas an electrodeposit of the same thickness may require 30 to 60 minutes.) Although a wide variety of materials can be deposited by electrophoresis, the deposits generally have been found to be nonadherent and to require subsequent processing such as mechanical working, chemical reduction, and sintering. Studies reported by Gebler[179,180] have indicated that electrophoretic deposition has potential for producing useful coatings.

Two recently completed investigations[183,185] have indicated that electrophoretic deposition of ceramic particles and electroplating of metals, conducted simultaneously in the same bath, have merit for producing cermet-type coatings for oxidation protection.

Huminik[185], in a program designed to provide erosion and oxidation protection to tungsten, tantalum, and molybdenum in the hot areas of rocket exhaust gases, made cermet deposits on all three metals. These deposits consisted of chromium boride, zirconium boride, zirconium nitride, molybdenum carbide, or titanium boride in a chromium matrix. The chromium-zirconium boride cermet coating (2 to 5 mils thick) gave the best over-all performance in oxidizing flame tests (3860 F), furnace oxidation (1 hour at 2000 F), and thermal-shock tests (0 $-$ 3860 F $-$ cold water quench). Life in the flame test varied from around 20 minutes to greater than 40 minutes.

Withers[183] made cermet deposits of nickel, chromium, platinum, rhodium, and cobalt-tungsten with Al_2O_3, ZrO_2, SiO_2, and $MoSi_2$. A Ni-ZrO_2 cermet coating (5 mils thick) protected molybdenum for 468 hours at 2000 F; a Cr-ZrO_2 cermet gave protection for 2-1/3 hours at 2500 F; and a Ni-SiO_2 cermet protected molybdenum for greater than 5 hours at 2500 F.

Chemical Reaction Deposition

Vapor Plating[33,186]. In the various modifications of the vapor-plating technique, also called gas plating and vapor deposition, a volatile compound of the material to be deposited is passed over the substrate which is heated to a temperature at which the compound is decomposed or reduced at the surface to form an adherent coating. The volatile compound can be reduced by hydrogen reduction, thermal decomposition, or displacement. Any material which meets the following requirements can be applied by vapor plating: (1) the material or its components must form a compound that can be vaporized at a relatively low temperature without appreciable decomposition; (2) the volatile compound must be sufficiently unstable to be capable of decomposition or chemical reduction at a temperature somewhat higher than its vaporization temperature; and (3) the material must not have an appreciable vapor pressure at the decomposition temperature.

The vapor-plating processes can be used to apply coatings of materials at temperature far below their melting points. Most of these processes can be carried out under either reduced or atmospheric pressure to give deposits which are often purer than coatings obtainable by any other method.

Detailed thermodynamic and kinetic studies have been carried out for only a few vapor-plating reactions; hence, the science of vapor plating, in contrast to the art, is in an early stage of development.

If the coating deposition is carried out at a high enough temperature, diffusion occurs simultaneously with the deposition, resulting in alloy or intermetallic formation.

The vapor-plating technique is not without its disadvantages. Difficulties are encountered in coating large or complex-shaped objects. These difficulties arise from nonuniform temperatures and gas flows.

An excellent compilation of information on vapor-plating processes is the book by Powell, Campbell, and Gonser[33].

Pack Cementation.[33,186-188] The term pack cementation, although improperly used, has become widely accepted as the designation for vapor-plating processes conducted in a sealed or semisealed retort. The technique overcomes much of the difficulty encountered in the regular vapor-plating technique, although troubles from nonuniform temperature and gas flow still can occur under certain conditions.

With some notable exceptions, the majority of the most promising coatings today are prepared by the pack cementation method. It is applicable to large complex shapes and is being used on a commercial scale. It is by far the coating-application technique on which the most research and development effort is being expended for the four principal refractory metals.

Essentially, the method consists of packing the article to be coated in a powder mixture contained in a retort, heating to the desired reaction temperature, holding at temperature for a sufficient time to produce the coating, and cooling down from the reaction temperature. The powder usually is a mixture of an inert material (e.g., Al_2O_3), the elements to be deposited, and an "activator" which generally is a halide salt which has sufficient vapor pressure to react with the elements to be deposited to form the volatile compound which can transfer the elements to the substrate. Sometimes the inert material is not used.

The process involves many variables which can greatly affect the average life and reliability of the coating system. Much of the information on the effects of the variables on the coating produced has not been published, although some information is becoming available under Government-sponsored programs.

Figure 16 shows the variation in coating thickness with time, temperature, and activator in the pack siliconizing of tungsten, as reported by Goetzel and Landler[47]. These investigators reported that, if the activator salt melts at the siliconizing temperature, there is danger of forming a discontinuous coating due to salt or filler inclusions. Alumina powders of different grain sizes were investigated as inert filler, but in most
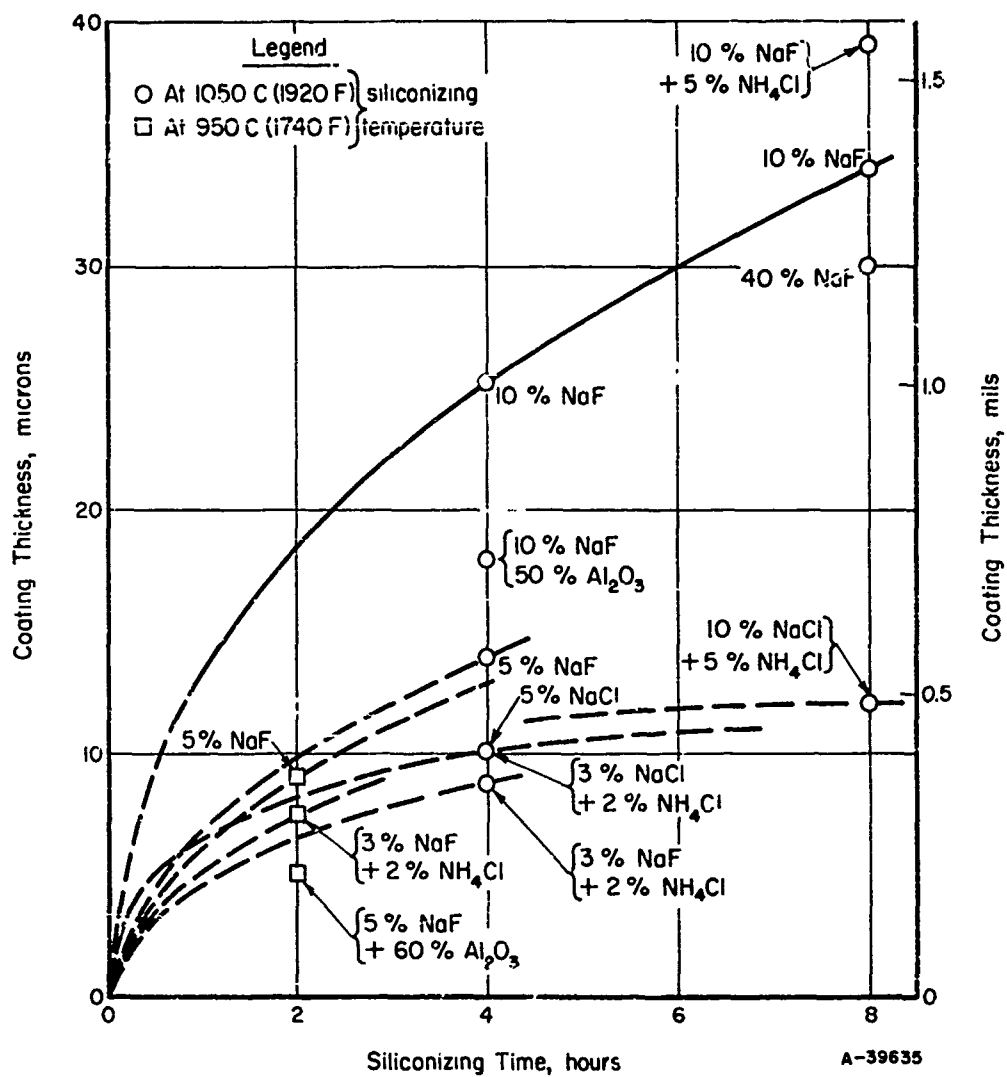
FIGURE 16. COATING THICKNESS VERSUS SILICONIZING TIME
FOR TUNGSTEN[47]

cases, these packs were inferior to packs without filler because the resulting coatings were thinner and more discontinuous.

Pranatis, Whitman, and Dickinson[189] subsequently confirmed the preference shown by Figure 16 for NaF as the activator in the siliconizing of tungsten, and presented the following calculated equilibrium pressures of SiX_4 for various activating agents:

Activating Agent	p (SiX_4) at 1050 C (1920 F), mm
NaF	0.79
KF	1.3
NaCl	0.001
KCl	0.0004

Klopp, Maykuth, and Ogden[190] also reported NaF as the preferred activator in the pack siliconizing of tantalum-base alloys. Using Al_2O_3 as a filler, they found a slight increase in deposition rate by increasing the silicon in the pack from 10 to 50 volume per cent, and no effect when increasing the amount of NaF from 1 to 8 weight per cent. Significant improvements in the protective life were obtained by application of the coating in two cycles instead of one, and by employing coarser-size Al_2O_3 in the pack which gave an increased coating thickness (3.5 versus 5 mils).

Exothermic Reaction. Work has been in progress for some time to produce cermets by thermite-type reactions of the following categories[192]:

(1) $MO_x + M' \rightarrow M'O_x + M$
(2) $SiO_2 + MO_x + Al \rightarrow Al_2O_3 + MSi_x + MO_x$
(3) $C + MO_x + Al \rightarrow Al_2O_3 + MC_x$
(4) $B_2O_3 + MO_x + Al \rightarrow Al_2O_3 + MB_x$.

These methods have recently been considered as possibilities for producing coatings on refractory metals; however, work has not been extensive enough to evaluate their potential for this application.[185]

Hot Spraying

There are three processes classified under the hot-spraying technique: flame spraying, plasma spraying, and detonation or flame plating. In these processes the substrate is kept relatively cool, and the coating materials in either the plastic or molten state are impacted against the substrate where they are quickly solidified. There has been a very large upsurge of interest in the hot-spraying techniques during the last few years, particularly in plasma spraying which features the highest temperatures.

In general, the coatings produced by these techniques are line-of-sight coatings, and as such the methods have not been applicable to coating complex configurations which have deep narrow recesses or internally exposed surfaces. In addition, the coatings tend to be porous and posttreatments are required (such as the glass impregnation of flame-sprayed Al_2O_3 used for the GE System 400[61]). Coverage and

porosity deficiencies also can be overcome to a certain extent by increasing the coating thickness; however, this also has its disadvantages.

Although there are recognized limitations on hot-spraying techniques for applying protective coatings to the refractory metals, some notable successes have been achieved by processes embodying these techniques in the cases of molybdenum[42] and columbium[44,61,268].

Flame Spraying. This process generally is conducted under oxidizing conditions, and is not so suitable for applying coatings to refractory-metal substrates as are systems involving reducing conditions. Several versions of flame spraying exist, using powders, rods, or wires which are formed into droplets in an oxyacetylene or oxyhydrogen flame.

The as-sprayed bond is almost entirely mechanical in nature[193], although in some cases, a chemical bond is believed to exist. The sprayed particles interlock with the mechanical projections and indentations in the substrate, the degree of roughness of which depends on the method used for surface preparation. Most of the sprayed particles which strike the surface are sufficiently plastic to conform to the irregularities of the surface and hence interlock with them. Almost all as-prepared flame-sprayed coatings have some porosity; in some cases this may be as great as 10 to 15 per cent of the coated area.[35] Galli et al.[35] reviewed and critically examined the flame-spraying process. Moore et al.[194] studied the mechanism of coating formation, mechanism of bonding, and stresses in flame-sprayed coatings.

Plasma Spraying. The theoretical and applied aspects of plasma spraying have been and are continuing to be under intensive study, and the MAB report[195] on plasma phenomena gives an excellent review of the varied aspects involved and the large number of groups working on the broad subject.

Plasma spraying can be used to form a coating from any solid material which will melt without decomposition. The extremely high temperatures available under neutral or reducing atmospheres makes the technique of particular interest where especially refractory materials or oxygen-sensitive materials are involved. Also, higher density and bond strength of the sprayed coatings have been reported as other advantages.[195] Company literature on operating procedures, equipment, and materials is available in considerable abundance.

Plasma spraying is not a simple technique, and the results obtained in a sprayed coating can depend on many factors. Mash, Weare, and Walker[197] presented the classification of process variables given in Table 17. Stetson and Hauck[198] reported on plasma techniques for spraying toxic and oxidizable materials. From preliminary studies it was concluded by Hayes and Johns[199] that it is feasible to develop metal-alloy coatings by spraying mixtures of metal powders with a plasma arc; however, much additional research is necessary. Studies on the effects of plasma spraying on the properties and stability of nonmetallic materials also have been in progress.[192,200]

TABLE 17. CLASSIFICATION OF PLASMA-SPRAY VARIABLES(197)

A. Plasma

1. Power input
2. Type of arc gas
3. Flow of arc gas
4. Plasma-torch geometry

B. Powder

1. Composition
2. Physical properties
3. Method of manufacture
4. Powder size
5. Particle-size distribution

C. Powder Feed

1. Type of powder feed system
2. Rate of powder addition to carrier gas
3. Type of carrier gas
4. Flow of carrier gas
5. Angle of powder entry into plasma
6. Location of powder entry port

D. Spraying Procedure

1. Torch-to-work distance
2. Traverse rate
3. Angle of torch with work
4. Cover gas
5. Spraying atmosphere

E. Substrate

1. Composition
2. Surface-preparation method
3. Surface roughness
4. Temperature

An interesting and significant observation was recently reported by Kramer, Levinstein, and Genier[200]. As-sprayed zirconia (on graphite) was characterized by fine cracks and apparently was heavily stressed. However, when zirconium boride was deposited as a thick dense layer and then submitted to a high-temperature oxidizing environment, it converted smoothly to an adherent nonspalling coating of zirconia which gave good protection under the test conditions.

Detonation or Flame Plating.[179,180,196] This process is based on the rapid controlled detonation of oxygen and acetylene in a gun chamber which heats the desired coating material (as a powder in a carrier gas) and then blasts the particles against the substrate at a very high velocity. The detonation-reaction front, which travels about 9600 feet per second at a pressure of 47 atm and 8000 F, impacts the particles against the substrate at about 2400 feet per second. During each explosion, of which there are about four per second, a 1-inch-diameter circle can be coated to about 1/4-mil thickness.

Other Application Techniques

This category of coating application, which includes vacuum metallizing, cladding, dipping, paint and sinter, slip casting, and hand troweling, should not be considered as a "catchall" category which contains all methods of minor importance. Several of these techniques, or modified versions of them, have been found to produce good coating systems.

Vacuum Metallizing. This technique has been widely used for producing extremely thin coatings by the evaporation, and subsequent condensation, of metal vapors produced by heating of the coating metal as a filament. Until recently, the method has been of little use for producing protective coatings for the refractory metals. However, a currently promising Cr-Ti-Si coating for columbium[201] can be prepared by using the basic technique of a vacuum and volatilizing the coating elements, but with the modification that the substrate is likewise heated with the coating elements so that diffusion occurs simultaneously with deposition. The process has been modified further by inclusion of an activator (KF) in the vacuum pack to permit lower operating temperatures and higher deposition rates. In essence, the latter version is a pack-cementation method using a pack which is under vacuum.

Cladding. Cladding techniques have been used for bonding oxidation-resistant alloys to refractory-metal substrates, but the method has its limitations as do all others. Roll and forge cladding involve deformation of the substrates, which is not always practical or desirable. Edge protection has been a problem which is normally attacked by welding. Cladding can also be accomplished by hot gas-pressure bonding without measurable deformation; this process has had extensive development in connection with AEC activities.[202,203] Although considerable work was done on the cladding of molybdenum during earlier investigations of the coating problem[41-43,250], at the present time, there appears to be only a small amount of interest in the technique for protection of the refractory metals from oxidation.

Hot Dipping. The application of coatings by dipping in molten metals has been long and widely used in industry for nonrefractory metals, and has been employed in several cases for the refractory metals. Depending on the coating system being produced and the time and temperature conditions used, diffusion to produce the desired coating compound may or may not take place in the molten metal bath. Frequently, subsequent heat treatments are employed. High rates of solution of the substrate in the molten bath and inclusion of dross in the coating to give poor reliability have been disadvantages in some instances.

Aluminum-silicon alloy coatings have been applied to molybdenum in a eutectic (12 per cent silicon) bath at temperatures of about 1550 F, covered with a cryolite-AlF_3-NaCl-KCl flux.[42] One process for coating molybdenum involves treatment in a molten copper-silicon bath which produces a silicide-base coating on the substrate; the coating has been reported to have given up to 200 hours of protection in air at 2900 F[206]. Oxx and Coffin[207] used a gold-silicon bath at 2550 F to silicide a previously prepared molybdenum capillary network on molybdenum and to fill the pores with the gold-silicon alloy; the coating system had some very attractive performance characteristics. Wlodek and Wulff[208] prepared dense, adherent, and ductile coatings of chromium on molybdenum by selectively freezing out the chromium solute from a supersaturated copper- or tin-rich liquid alloy. Under the most favorable combination of supersaturation, nucleation, and mass transfer, coatings as thick as 4 mils can be obtained.

Dipping in an aluminide-base bath has been used extensively to screen a wide variation of compositions for coatings on columbium and tantalum-base alloys.[209,210] Carlson[203] used an Al-15Si bath to coat several columbium-base alloys in the temperature range of 1500 to 2100 F; optimum coatings were obtained with a 3-minute dip time at 1690 F, followed by a treatment in vacuum for 1 hour at 1905 F.

Paint and Sinter or Diffuse. The ceramics and enameling industries have been using the paint and sinter technique for a long time, and in these applications, the art is well developed. The applicability of the technique for the production of protective coatings on refractory metals has been investigated at various times with varying degrees of success.[42]

Major interest in the technique has recently been generated primarily as the result of work done by the General Electric-McDonnell Aircraft program on the use of refractory alloys as structural materials in re-entry or boost glide vehicles.[211-213] The aluminide-base coating (designated LB-2) which emerged from this program was used to protect a complex fin-rudder assembly of F-48 columbium alloy. The application method involves dipping, painting, or spraying two different slurries, followed by a 1-hour diffusion anneal in purified argon. The base-coat slurry, which consists of Al-10Cr-2Si alloy suspended in an acetone-xylene vehicle, is applied and allowed to air dry for 1 hour. Then the top-coat slurry, consisting of Reynolds aluminum paste suspended in an acetone-xylene vehicle, is applied and air dried for 2 to 24 hours, after which the diffusion anneal is carried out. Both slurries require thorough mixing before and during use to prevent the suspensions from settling out.

Adherence, Uniformity, and Continuity in Coating Systems

Closely allied with the use of the different techniques for producing coating systems are the aspects of adherence, uniformity and continuity. These were subjects of much concern before refractory metals came into prominence, and they remain problems of varying degrees of magnitude, depending upon the system under consideration, its technique of being put together, and the mission it must accomplish. These aspects are heavily involved in the reliability of the system.

Achieving and maintaining a uniform coating frequently depends on close control of the known process variables, constant alertness to discover unknown and uncontrolled variables, and a full realization that the systems being produced are extraordinary in nature and that they require meticulous attention.

Additional research needs to be done to identify the causes of discontinuities in coatings and to find procedures to overcome this constant source of trouble. Why, for example, under conditions of excellent physical and chemical cleanliness and with the coating process under rigid control, will coating systems fail at randomly located, localized areas which are not centers of macroscopic stress concentration? Faust[11!] and others have commented on this situation, particularly with respect to electroplates; it is common in other types of coatings also. It is thought that a major factor involved is mechanical cleanliness of the substrate surface. According to Faust, when mechanical operations are performed on the substrate, the surface is distorted, strained, torn, and smeared. Such a surface has the appearance of a plowed field even for a smoothness of 3 to 5 microinches rms. The lack of specification of mechanical cleanliness causes many discrepancies in attempts to repeat results reported by others.[115] The effect of a small but critical amount of disturbed or worked surface metal on the quality obtained in gas nitriding of stainless steel was recently reported by Coppola.[214]

In a broad sense there are two types of coatings, diffusion and nondiffusion (or claddings). Diffusion types of coatings have fewer difficulties with adherence or bonding between the coating and substrate than do nondiffusion coatings because they are grown from the substrate. Ways and means of promoting better adherence in nondiffusion coatings are always desired.

The coating of metals with ceramic materials is a well-established commercial practice, but two reviews by Van Houten on ceramic-to-metal bonding[215] and the bonding of cermets to metals[121] indicate that the attainment of good adhesion is still as much of an art as it is in nondiffused metallic coatings. There is evidence, however, that a science of adhesion is evolving.[216-218]

The work by Moore and Thornton[219] on the effect of oxygen on the bonding of gold to fused silica is clearly a matter of interest in understanding adhesion and bonding. Pellets of gold adhered to silica surfaces when heated in air or oxygen but not when heated in vacuum. When bonded specimens were shear tested, fracture occurred in the silica rather than at the gold-silica bond. This and other circumstantial evidence suggested that gold might form an oxide which diffused into the silica. More recently Shishakov[220] has given rather convincing evidence for the existence of a gold oxide. These findings fit in well with those of King et al.[216], who found that strong chemical bonds developed between porcelain enamel and metal only when the enamel at the interface was saturated with the ion of the metal in contact with the enamel. Surface

roughness was not necessary for excellent adherence, although it was found to improve the apparent adherence when the bond between the enamel and metal was relatively weak.

In this same channel of thought, it is believed that the GE System 400 coating (flame sprayed Al_2O_3 impregnated with a glass) on columbium has excellent chemical bonding because of an epitaxial fit of oriented CbO at the interface.[61,268] An annotated bibliography of epitaxial growth was recently compiled by Abbott.[276]

It would appear that attempts to apply this mechanism of adherence to other non-diffusion, nonmetallic coatings on the refractory metals would be in order, because many of these are now said to be bonded nearly totally by mechanical interlocking.

Reliability

Because the need for highly reliable coating systems has become so great, establishment of reliability by the use of sound statistical procedures is rapidly becoming a vital aspect of the technology of protective coatings for the refractory metals. Statistics is being used in designing experimental programs to evaluate different coating systems and to analyze the results obtained from these programs. Because of the number of variables involved in coating processes, there is a strong trend toward using statistical procedures to optimize these processes and to establish reliability levels for the coating systems produced.

It is significant that the Air Force has recently sponsored three programs having major phases to optimize pack-cementation-coating processes and determine reliability levels by using statistical designs of the experimental programs.[221-223] Two of these are for molybdenum (Chromalloy W-2 and Pfaudler PFR-6 coatings) and the third is for columbium (Vought coatings). Variables collectively considered for study in these programs are: purity, particle size, and distribution, age, mixing, density, and composition of the pack; soundness and surface preparation of the substrate; composition and sealing of the retort; pressure in the pack; and processing time and temperature.

There are three points which need to be made regarding programs of this nature.

First, with respect to a particular test criterion for a coating system (e.g. coating life under a fixed set of conditions), what results is an average numerical value of the property under consideration and a standard deviation which is a measure of the scatter in the experimental results. From these two numbers, there is a temptation to assume a normal distribution and to quote a tolerance or confidence limit above which some percentage of the values obtained from a statistical sample can be expected to fall. This can lead in some cases to a large degree of overconfidence because such limits can only be established properly by first determining the type of distribution which the data follow. Assumption of a normal distribution when the data in fact would follow an extreme-value distribution, for example, would allow a higher tolerance limit to be stated than would be justified. One of the reasons for the assumption of a normal distribution is that a very large number of data are needed to accurately determine the tails of distribution curves, which are of vital concern when establishing tolerance limits.

The second point which needs to be made involves a word of caution in the use of reliability data for design purposes. Such data are usually derived from a laboratory type of specimen under laboratory conditions of preparation and testing. Extrapolation to actual service conditions and actual hardware of larger dimensions and more complex geometry can be very dangerous indeed.

The third point requiring attention relates to the definition of realistic criteria fo evaluating coating systems and the proper interpretation of data resulting from evaluation programs. This subject has been presented well by Graham, Luft, and Sayre[5], whose remarks are so appropriate that they are quoted below:

"Refractory metal coating development has often been concerned with just the protection of the refractory metals with insignificant consideration for useable statistical results. A criteria analysis of several limited tests on oxidation resistant, coated molybdenum and columbium will be discussed in order to demonstrate approaches which might give design engineers more useful data. Although this work[171] has barely explored the relationships of various refractory coatings tests, a discussion of such approaches is expected to encourage others to pursue such work, and in greater detail. Figure 17 shows the test results of four commercial coatings for molybdenum that have been evaluated under combined thermal shock and flexure conditions. Specimens were cycled by heating to 2200°F., cooling to 1000°F., and reheating to 2200°F. in two minute cycles. At this same time, the thermal shock specimens were cyclically flexed at 1,725 cycles per minute by reverse bending to a maximum deflection which produced 10,000 psi outer fiber stress at a temperature of 2200°F. Due to limited funding and relative high specimen cost, only two specimens of each coating were evaluated. The lowest line on each bar indicates the number of thermal shocks before the molybdenum began to oxidize, as was determined visually. The total bar length represents the maximum life to specimen fracture. An indication of the consistency of life between two specimens of each coating is beside each coating bar graph. The consistency value was established by averaging the life of each coating pair and calculating the percent deviation from average. It is recognized that the use of only two specimens limits the statistical validity of these tests, as is the case in most coating tests to date.

"Slightly different test conditions or criteria can affect the relative merit of one coating over another. Figure 18 shows the results of another test on some of the same coatings reviewed above. The tests[256], made at the Naval Air Material Center, Philadelphia Navy Yard, were made on 9" long specimens stressed to 45,000 psi tension in a 4 inch hot zone at 1800°F. The specimens were quenched by cold air every 35 minutes which cooled them to 150-200°F. in 1-1/2 minutes. The tests were terminated at failure, or at about 500 cycles.

"In these tests, a different interpretation results from the test program. It is observed that any coated specimen that met the 500 cycle test did meet the criteria. The several coatings had different capabilities of meeting the established criteria. Of the five coatings tested, only pack deposited molybdenum disilicide coating exhibited 100% reliability in that all four of the specimens successfully resisted failure. The plated chromium with alumina coating, which had the longest life and best consistency in the previously discussed test, had a 75% reliability factor, in that of four tested specimens, only three met the test criteria. The multilayered, electroplated Cr-Ni coating had a 25% reliability factor, while a thinner, electroplated Cr-Ni coating had a zero reliability factor. The flame-sprayed and diffused Al-Cr-Si coating also had a zero reliability factor.

"If the criteria had been 100 cycles, all coatings would have met a 100% reliability factor. If the criteria had been 1,000 cycles, (it is possible that) none of the tested coatings may have met usable reliability standards."[5]
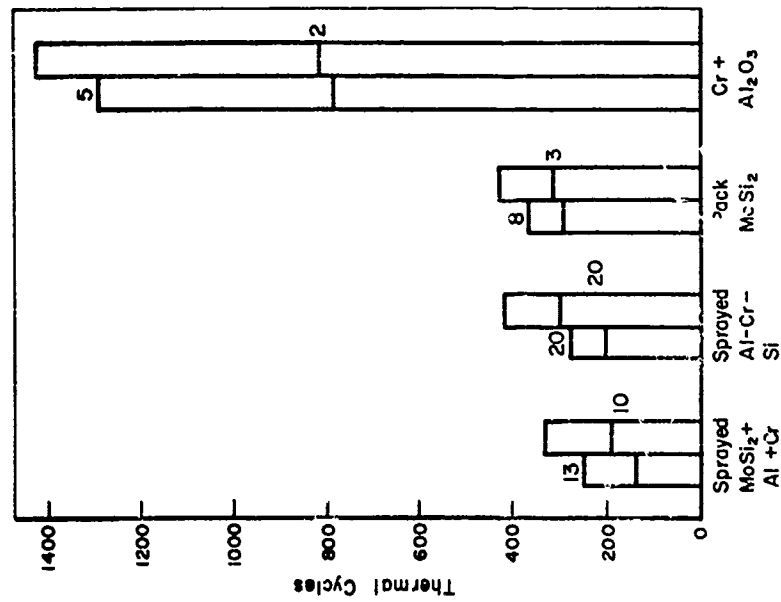
FIGURE 17. LIFE OF COATED MOLYBDENUM UNDER THERMAL SHOCK PLUS FLEXURE(5)
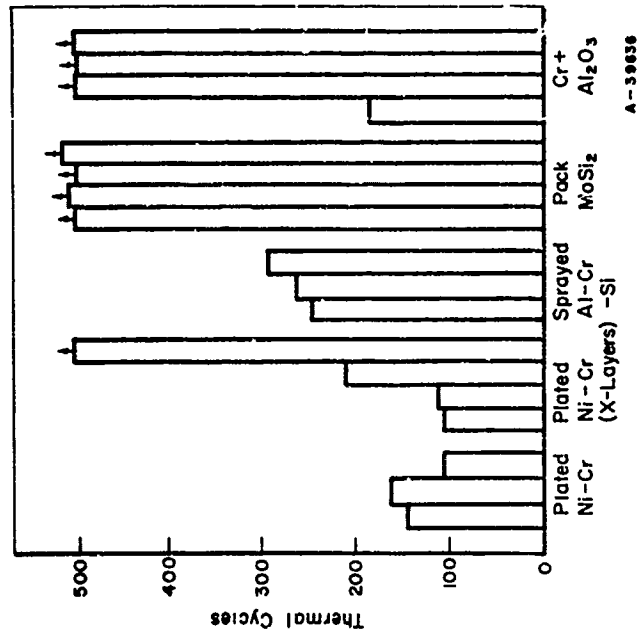
Shock conditions: 1000 to 2200 to 1000 F, 2 minutes.

FIGURE 18. LIFE OF COATED MOLYBDENUM UNDER THERMAL SHOCK PLUS 45,000 PSI TENSILE STRESS(5, 256)

Shock conditions: 150 to 1800 to 150 F, 35 minutes.

Another aspect in comparative-evaluation programs is that indicated by Seelig[171]. It is important, when comparing coatings under specific test conditions, that all tested coatings be specifically developed for the particular thermal exposure to which they will be subjected. It is known that such factors as coating thickness, diffusion temperature, and preheat treatment for bonding can all be effective in changing the relative order of merit when the test criteria are changed. A coating system with fixed physical properties could be designed to be superior in one thermal environment, but it also could be designed, by modifying process conditions slightly, to be inferior in the same thermal environment.[171]

EVALUATION PROCEDURES FOR COATING SYSTEMS

Procedures and techniques for evaluating coating systems are about as plentiful as the number of organizations working on the problem of protecting refractory metals. There are no standardized tests to which coating systems are subjected; consequently, comparison of results from different organizations is sometimes impossible, always difficult, and frequently dangerous and misleading.

There has been a continuing awareness of this situation on the part of workers in the field, and many discussions have been held concerning it. A subgroup of the Refractory Composites Working Group has been continuing to study the problem. There are indications that some progress is being made; although, due to the complexity of coating systems and diversity of types of hardware to be protected and missions to be accomplished, the progress is expectedly slow. [179,180,224]

The Air Force has recently initiated a program to develop standardized test techniques for the meaningful evaluation of coated refractory-metal alloys. The techniques which will evolve from this program are intended for coatings which are ready for production application. The effort is being conducted in three phases: (1) information, test techniques review, and establishment of environments to be simulated in tests; (2) establishment of laboratory-type test techniques to simulate important end-use-condition parameters, and (3) conduct tests on existing coatings for refractory-metal alloys and statistically evaluate the data in terms of categorizing various coatings for aerospace applications.

The surface has hardly been scratched as far as any standardization of testing techniques for research and development programs is concerned. In the past, most of these programs have followed a familiar testing pattern, using small coupon or rod specimens except where special shapes are needed (e.g. tensile specimens):

        (1) Static oxidation
        (2) Cyclic oxidation
        (3) Thermal shock
        (4) Bending
        (5) Oxidation under stress
        (6) Erosion
        (7) Impact
        (8) Combinations of tests to simulate service conditions
        (9) Evaluate in service.

A very large number of experimental coating systems are discarded by the time Step (3) is completed.

Major references to recently used or developed techniques for evaluating properties and performance of coating systems are summarized in Table 18. There are many parameters in most of these tests, and in general each group of workers chooses those values of the parameters which seem best-oriented toward the end objective of the particular program at hand and/or which are convenient.

Aves[261] recently presented the following outlines for screening tests, proof tests, and nondestructive tests for coating systems:

TABLE 18. REFERENCES TO RECENTLY USED OR DEVELOPED TECHNIQUES FOR EVALUATING PROPERTIES AND PERFORMANCE OF COATING SYSTEMS[a]

Property or Performance Evaluated	35	41	42	43	44	46	48	49	61	67	117	137	143	171	172	183	184	191	201	207	209	213	222	223	224	225	227	228	229	230	231	232	233	234	236	250	261
Adherence	X																													X						X	
Combination testing			X	X	X									X	X				X		X			X		X					X	X		X	X	X	X
Defect tolerance				X	X															X	X																
Ductility																																					
Bending	X		X	X	X											X	X		X	X	X		X	X		X					X	X		X		X	
Tension	X		X		X											X	X		X	X	X		X	X		X					X	X	X	X			
Emittance													X																			X					
Erosion (abrasion)	X		X	X					X					X												X	X		X		X				X	X	
Fatigue (mechanical) testing																																					
General evaluations	X	X	X						X					X	X			X	X	X	X		X	X		X	X	X			X	X		X		X	X
Impact	X		X											X	X			X	X							X	X										
Inspection																																					
Cracks and defects																		X				X						X									X
Porosity	X																	X										X								X	X
Oxidation																																					
Heating																																					
Induction																			X	X	X					X					X	X		X			
Plasma gun				X						X									X	X	X			X	X	X					X	X	X	X			
Radiant						X			X										X	X	X		X	X	X	X								X			
Self-resistance						X	X	X	X								X					X															
Torch	X			X						X							X		X		X				X	X						X	X	X	X	X	
High-velocity gas flow	X																																X	X			
Low pressure																																X	X				
Stresses in coating systems																	X																				
Thermal cycling	X	X	X	X	X				X		X	X		X	X	X	X		X	X	X		X	X		X										X	
Thermal shock	X	X	X	X	X				X		X	X		X	X	X	X		X	X	X		X	X		X									X	X	

(a) See also the summary reports on the annual meetings of the Refractory Composites Working Group for a large assortment of testing techniques[179, 180, 226], and Volumes II through VIII of WADC Technical Report 59-744[235].

Screening Tests Used to Evaluate High-Temperature Cementation-Type Coatings
on the Refractory Metals(261)

Test	Factors Evaluated
Thermal cycling static oxidation in air	Oxidation resistance Thermal shock resistance
Thermal cycling sustained load	Effect of coating on ductility of substrate Effect of specimen creep on the coating integrity Thermal-shock resistance Oxidation resistance
X-Ray diffraction	Coating structural analysis
Plasma arc or oxyacetylene torch	Coating emissivity Thermal-shock resistance Oxidation resistance Melting point
Bend	Coating adhesion Ductility
Tensile	Effect of coating or processing on substrate strength Ductility Elongation
Metallographic observation	Substrate structure Coating structure Coating thickness Bond characteristics Detection of inclusions
Microhardness traverse	Cross-sectional hardness of coating and substrate Effect of processing on substrate ductility
Electron-microscope inspection	Detection of injurious inclusions in substrate or coating
Fatigue	Effect of coating or coating process on substrate fatigue properties Fatigue strength of coated-metal system

Proof Tests Used To Evaluate Coated Structures Under Simulated
Operational Conditions(261)

Test	Factors Evaluated
Ram jet	Thermal shock resistance, vibration resistance, erosion resistance, oxidation resistance, and structural integrity evaluated simultaneously over a representative time-temperature profile (i.e., glide re-entry profile)
Blow pipe	Same as for ram jet except for some variations
Quartz lamps	Simulates the effects of aerodynamic heating on a desired configuration
Plasma arc	Can be programmed to follow a desired time-temperature profile determining variations of the factors evaluated in the ram-jet test, vibrations and erosion excluded
Rocket blast	Evaluation of coating under exceptionally severe thermal-shock conditions (air temp to 4000 F in 1 second)

Nondestructive Test Techniques For Use In Testing Cementation-Type
Coating Integrity Before Service[261]

Test	Reliability	Versatility	Purpose of Test
High-temperature controlled oxidation followed by magnified visual observation furnace equipment	Good	Excellent	To determine coating flaws by observation of through-coating oxidation To determine weakness existent in bond strength due to thermal shock
Evaporgraph	Under investigation		To indicate coating discontinuities on flat-panel surfaces Unsuitable for determining edge or corner defects
Electromagnetic inspection	Under investigation		To detect porosity, cracks, and pits Unsuitable for determining corner or edge flaws
Ultrasonic inspection	Poor	Poor	To detect surface and subsurface flaws Unsuitable for use on thin skins or in determining corner or edge defects
Fluorescent particle inspection	Under investigation	Good	To detect surface cracks, pits, and similar coating defects
Red dye penetrant	Under investigation	Good	To detect surface flaws in coating
Radiographic inspection	Poor	Poor	Sensitivity difficult to control for detecting small coating flaws in assembled structures
Visual magnifying glass	Poor	Good	Not as suitable or reliable as when performed after an exposure test

Aside from the problem of standardization of evaluation procedures, there are other problems of considerable importance. One of these is defining the service requirements; in several cases these are not now well understood. Assuming known service requirements, how can they be simulated in the laboratory so that meaningful and translatable evaluation data can be obtained?[5]

One of the problems along this line is that of obtaining the high test temperatures required for evaluating coating systems, especially those involving tungsten. Self-resistance heating or induction heating is usually resorted to, but there can be dangers involved in using these techniques. In service, most of the applications involve exterior heating, and the stress-distribution pattern in the application can thus be different from that evaluated in the laboratory. Differences in performance have been observed for coated tantalum, for example, evaluated using self-resistance heating and radian heating.[209] The possibility of increased diffusion resulting from induction heating was mentioned earlier in discussing diffusional compatibility. Some investigators have taken precautions against this possibility by using a susceptor, which simultaneously supplies the necessary heat by radiation. Quartz pencil lamps are finding increased use for temperatures below 3000 F. Oxyacetylene torch testing has been used frequently as a convenient technique for reaching high temperatures and simultaneously having a blast of hot gas hitting specimens. Depending on the particular experimental arrangement, results obtained can be misleading because the torch can be centered on a flat surface which generally has longer life than an edge.

In summary, it not only is a difficult problem to produce a good coating system, but it can also be difficult to evaluate it properly and be able to assess its virtues and shortcomings relative to the current state of the art and, more importantly, relative to the requirements for accomplishing the intended mission.

PROTECTIVE-COATINGS RESEARCH AND DEVELOPMENT

References to recent and current major surveys of protective-coating systems of the refractory metals are tabulated below.

General	Mo	Cb	Ta	W	V
5	41	14	45	47	238
239	42	201	240	48	
	173	211	243	50	
	211	223		51	
	240	240		240	
	241			243	
	242				
	243				

Because of the large research and development activity at the present time, all surveys and reviews, including this one, become at least slightly out of date by the time they are disseminated.

Master Compilations of Information on Protective Coatings

Tables 19 and 20 are master compilations of information on protective coatings prepared from completed questionnaires returned to the Materials Advisory Board Subpanel on Refractory Metal Protective Coatings. The National Academy of Sciences – National Research Council, through the Materials Advisory Board, sent out these questionnaires in July of 1960 to about 100 individuals or organizations known to be concerned with the problem of protecting the refractory metals from oxidation. Replies were received through February of 1961. To the information contained in the replies, additions and revisions have been made as warranted by later documents submitted to the Defense Metals Information Center from various organizations having active programs. References to published documents or currently active contracts have been made where possible. For some of the coating systems more extensive information is available than is given in the compilations. Some of this information is presented in later sections.

Table 19 contains general information on the reported status of coatings, method of preparation of the coating systems, importance of substrate preparation, as-applied coating composition and thickness, maximum reported temperature and time for protection, and general remarks on applications, shortcomings, and special properties. Table 20 gives a more detailed account of the performance of the coating systems under oxidizing conditions. The primary breakdown is by basic coating material, and secondary breakdown is by coating application method.

Research and development effort has been in progress for the longest period of time on coatings to protect molybdenum from oxidation, and by far the largest amount of work has been done in this area. Many of the coating shortcomings found for molybdenum also have been found for the other refractory metals. Many of the organizations which have been working on protective coatings for molybdenum have also been considering coatings for columbium, tantalum, and tungsten with varying degrees of effort. Discussion of coatings will be done by coating-base classification for each of the refractory metals.

TABLE 19. MASTER COMPILATION OF GENERAL INFORMATION ON PROTECTIVE COATING SYSTEMS

TABLE 19. (Continued)

TABLE 19 (Continued)

Intermetallic Coating: Silicide Base (Continued)

Organization	Name of Coating	Reported States of Coating				Metal or Alloy Base Substrate					Plating from Solution		Chem Reaction Deposition		Coating Applied on Method										Preparation of Substrate						As Applied Coating Composition	Coating Thickness mil	Maximum Reported Temp and Time of Protection of Substrate				Remarks
		Research	Developmental	Semicommercial	Commercial	Mo	Cb	Ta	W	Fused	Aqueous	Electrophoretic	Vapor Plate	Pack Cementation	Flame	Plasma	Vacuum	Metallic, E	Hot Spraying	Clad	Dip	Paint & Spray	Other Methods	Critical	Partial	Recommended/Preferred	Unimportant	None			Temperature °F	Time Hr	Min	
Intermetallic Coating: Silicide Base (Continued)																																		
Chance Vought Aircraft Inc.(221,226)	height's, IX	x	x			x								x										x					Coating compositions consist of two or more of following (excluding substrate): Si, Cr, Al, B, Ti, Cb, C	1-35	2800	8			Multicycle pack cementation often used. Plant arc diffuse method being employed to touch up accidentally damaged areas of coatings. Coating not as ductile as desired. Self-healing at temperatures over 1520 F.
	Vought Si Cb, Si Cb		x				x							x										x					Coating consists of a most under metallics including Be, also silicides and silicides. Carbon	1-35					Where Si will oxidize for use in coating self-healing characteristics under AF 33616-7896. Coatings for Cl being optimized under AF 33616-7896.
			x											x										x					being used currently as a coating for 4-10 min static and operation condition, necessitating a pre-determined corrosivity erosion resistance ductility etc. often require silicon. The coating system (use of high temp inert gas diffusion treatments, and surface overlay applications of bi-flame and plasma spray), fitch pots and silicon sprays when desired	1-35					
Chromalloy Corporation(221,226)	Nr2	x	x		x									x												Important			Proprietary	0.5-3.5	-	-	-	Environment test 2000-4000 F. Up to 7200-hr protection reported at 2000 F. (tensile ability for Si-20). Continuous oxidation resistance with temp. Self-staining properties good at approx 2600 F. Coating is intermetallic, and brittle at room temp. Fairly expensive but large scale use coverresults in dust, price reduction. Currently being used severely.
	T 2	x	x		x									x												Important			Proprietary	0.5-3.5	-	-	-	
	W 2	x	x		x									x												Important			Proprietary	0.5-3.5	-	-	-	components, probes, tips, tail pipes. Process currently being optimized
Tapco Aerosystems Company(286,235)	Chromalloy # 2	x	x		x									x										x		Important			Proprietary	24	-	-	-	Best of 30 coatings evaluated from standpoint of reproducibility. Good oxidation life, poor on chambers and nicon of 10 mils or less good on ratio of 30 mil.
Langley Research Center, NASA(214)	Chromalloy # 2	x	x		x									x										x		Critical			Proprietary	1-2	2600	20		See NASA Technical Note D-117 for considerable additional information
North American Aviation, LA	Chromalloy W 2		x																										Unknown	-	2600	25		At 2750 F, coating reacted with alumina binder, magnesia and zirconia sometime holders.
Chromizing Corporation(226,235)	Durak B	x	x		x									x										x						2-00	80		Preliminary tests and initial experiences indicate superiority over earlier coatings from company with respect to reliability reproducibility service life, and tolerance for surface imperfection on substrate. Total emissivity 0.14-0.15 1700-2600 F 0.55-2960 to 3140 F
Pfaudler Company(221,226)	PFR 5	x			x									x										x		Critical			Proprietary Mo Cr Si	2-15	3300	65		Diffusion stability and self-healing properties good at 3300 F
	PFR 6		x											x															Silicide + other intermetallics	-	-			Diffusion stability good, self-healing properties good currently being optimized

TABLE 19 (Continued)

Organization	Name of Coating	Reported Status of Coating			Coating Application Method																		Preparation of Substrate				As-Applied Coating Composition	Coating Thickness mils	Maximum Reported Temp and Time of Protection of Substrate			Remarks
		Accepted	Developmental	Exploratory	Commercial	Metal- or Alloy-Base Substrate			Fused	Flame	Electrophoretic	Vapor Plate	Pack Cementation	Flame	Plasma	Vacuum	Detonation	PTC	Pack & Slurry	Dip	Brush	Other Methods	Chem.	Flame	Plating	None (Unsupported)			Temperature, °F	Time hr	min	
Intermetallic Coating: Silicide Base (Continued)																																
Plansee Company (222, 223c) (Continued)	PFR-7	x					Cb	Ta	W					x										x			Silicide + other materials	3-5	3000	95		Diffusion stability satisfactory, self-sealing properties good
	PFR-8	x					Cb	Ta						x										x			Silicide + other materials	3-4				Diffusion stability satisfactory, self-healing properties good
	PFR-9	x					Cb	Ta						x										x			Silicide + other materials	2-3.5				Diffusion stability satisfactory, self-healing properties fair
Picatinny Arsenal (196)	Molybdenum Disilicide	x					Mo						x															Proprietary	1-4	4000	100		Among best 5 out of 23 materials and coatings evaluated for possible use on a hypersonic glide for a leading-edge application at $M=8.5$. Certain oxidation studies showed quality of coating
Solar Aircraft Company	SiH-770		x				Cb	Mo																	x			WSi₂	5.25(?)	2000	>10		Coating in brittle and cracks accelerated oxidation "pest" problem at 1200-1900 F
New York University (46, 47)	Disilicide			x			Cb														x				x			Al-Si	0.5-7	3300	15		Ceramic. Silicide at or below oxidation temperature. Not self-healing below 2000 F
National Research Corporation (40, 255)																																
Linde Company (44)	LM-5		x				Cb	Ta	W				x		x					x	x				x			40Mo-40Si-10Cr-8-1Cr	4-6	2400	500		Not now generally offered for sale by Linde. Some loss of Si and application to hardware. Also applied by Linde flame plating process. Self-healing protection good over 1800 F. Cannot coat complex shapes by present methods. Difficult to apply or impractical to use on thin sheet
Union Carbide Metals Co. (44)	LM-5 + ...			x			Cb	Ta													x		x	x			Cr-Si base coat 44Cb-37Ti-19Cr-5V (A)	3				Silicic oxidation resistance of LM-5. Undercoat improves self-healing and thermal shock properties
General Electric Research Laboratory (260)	Liquid Phase Coating	x	x				Cb						x			x						x		x			50Mo-33Ru-19Si(Mo)₂, on a continuous matrix of Au-Si alloy)	5-20	2500	1000		Less than 1 mil at 1000-1500 F. Heating and cooling through range does not affect life in reverse. Liquid phase gives self-sealing. Interdiffusion limits life. Application method is hot dip and slip cast and/or spray and sinter
Metal Treat Plansee A,C (286)	Silicide Coating	x					Cb							x										x			Silicides					
Intermetallic Coating: Miscellaneous Base																																
Avco Research Laboratory (264-277)	Zirconium Boride	x					Cb							x									x	x			Various CY-2 in sintered or hot press (using coatings) Ti + Al	~3-5	2000	100		ZrO₂ (plus ternary oxides) on surface after oxidation exposure. Self-heating properties excellent. Max temp ~2850 F. Reported in achieving at r at elevated temperatures
Brush Beryllium Co.			x	x			Cb																	x			M₃Rh₁₃ or MRh₁₂	2300		>5 (hrs)		Research on coating techniques and degree of protection afforded is in its infancy
Picatinny Arsenal (196)	Zirconium Diboride	x					Cb						x															ZrB₂	10	4000	1		Among best 5 out of 23 materials and coatings evaluated for possible use on a hypersonic glide for a leading-edge application at Mach 8.5

TABLE 19. (Continued)

TABLE 20 MASTER COMPILATION OF INFORMATION ON PERFORMANCE OF COATING SYSTEMS UNDER OXIDIZING CONDITIONS

Organization	Name of Coating	Metal or Alloy Base Substrate Mo Cb Ta Ti W	Continuous Oxidation at Life hours Temperature F 1600 2000 2100 2162 700 2200 2400 2500 600 2700 2900 3000 3270 4000	Contamination Resistance	Diffusion Stability	Self Healing Properties	Results
Metallic Coating Fe, Ni, Co base							
National Bureau of Standards[245]	Electrodeposited Cr Ni	x	>40			Poor	Separations with cooling when thermocycled
Thiokol Chemical Corp., Reaction Motors Div		x	200		Fair		Post-fire Unsuitable for long periods above 2000 F.
Alloson Division, GMC	CMP Coating for Mo	x	1300		Undercoat of chromium prevents diffusion	Shows some tendency toward self healing	Coating is relatively soft, and thus not too erosion resistant. Deforms to provide sharp corners
Nuclear Metals, Inc.	Stainless Steel	x x					Shortcoming is thermal expansion mismatch
Wall Colmonoy Corp		x x					Melting or oxidation from base
Metallic Coating: Noble and base							
American Machine & Foundry Co[161]		x			Excellent	Poor	Coatings failed by particle formation rather than by oxide consumption or diffusion
Thiokol Chemical Corp. Reaction Motors Div		>	10-20 500 ~10	Good	Good	Good	Unsuitable for long periods above 2500 F
Quantex Inc		x	900		Good	Good	Sharp edges cause failure. No failure on flat or rounded surfaces
Wad Nickel Co. Ltd[248]		v	100-hr		Good	None	Shortcoming is thermal exposure mismatch
Metallic Coating: Miscellaneous metal base							
General Electric Co., FPLD[171 172]	GE System 300	x	600 240 90 300 >6 >4 ~7	High	High, 2700 F	Very little	Can withstand 500-1000 cycles RT to 2700 F plus 90 hr static exposure at 2700 F Also 22 cycles RT to 3000 F plus 1.5 hr static exposure at 3000 F Ultimately fails by thermal stress cracking of Cr plate
Climax Molybdenum Co., Inc[249]	Al-Cr-Si	x					Exhibited no plastic flow yet MoO₃ or atmosphere
Picatinny Arsenal[196]	Al-Cr-Si	x		<150		Moderate	Observed above 2500 F Being further developed under AF33(616)-7215
Thompson Ramo Wooldridge, Inc[201]		x					Life shortened in presence of high layers of MoO₃ in atmosphere
Intermetallic Coating: Aluminide base							
Pratt & Whitney Aircraft, Canel		x				See remarks	A degree of self healing is certain in certain substrate combinations
General Electric Co., FPLD[211 212]	L-8-7	x	>2	Excellent	~30 hr life at 2500 F	See remarks	
McDonnell Aircraft Corp[211 212]	Aluminized Cb fusion coating	x	2 10	>2 hr at 2500 F	>2 hr at 2500 F	Little if any	Can withstand deformation and severe thermal shock.
Sylvania-Corning Nuclear Corp[209 210]	C-14	x	10 10				Can withstand deformation and severe thermal shock.
	1945 Al-Si-Y	x				Good	Withstands deformation and severe thermal shock. Severe self oxidation reported under AF 33(615)-1462

TABLE 20 (Continued)

Organization	Name of Coating	Metal or Alloy Base Substrate				Continuous Oxidation Life, hours — Temperature, °F	Contamination Resistance	Diffusion Stability	Adhesive Properties	Remarks
		Mo Cb Ta W								
Interrelate Coating — Silicide Base										
Brush Beryllium Co										
Pfaudler Industries Inc		x x					Excellent	Excellent	Excellent	
Thiokol Chemical Corp — Reaction Motors Div		x x					Good	Good	Good	
Vitro Laboratories		x							Yes, since 1500°F	
Fansteel Metallurgical Corp — W-2 Silicide		x					Excellent	Excellent	Fair	
Battelle Memorial Institute										
Boeing Airplane Co — Seattle		x x						Good	Good over 90°F	
Chance Vought Aircraft Inc —		x x						Exc. over 2000°F	Good over 1500°F	
Chromalloy Corporation 2717		x x						Good	Good at 2000°F	
Bell Aerosystems Co		x x					Depends on material in contact with coating	Fair	Good at 1 — 6 hrs	
Langley Research Center NASA	Astrolloy #9	x								
North American Aviation LA		x								
Chromizing Corporation		x								
Pfaudler Company —	PFR-5 PFR-6 PFR-1 PFR-3 PFR-6	x x x x x					Good Good Good Good	Good Good Satisfactory Satisfactory Satisfactory	Good Good Good Good Fair	
Plastonics Institute	Molytherm Drislloy	x x					Good	No contents above	Excellent	
Sylvania Electric Company	Sil-per	x						State 2500 and 3000°F	Average over very	
New York University	Drislloy									
National Research Corporation		x								
Linde Company	LVS	x x						Good	Good over 1500°F	

TABLE 20 (Continued)

COATINGS FOR MOLYBDENUM

Coatings for Molybdenum

Metallic Coatings

Fe, Ni, Co Base. Much work was done on the use of Fe-, Ni-, and Co-base alloys as coatings for molybdenum in former years when the temperature requirements were much lower than they are today and when less was known about the intricacies of refractory-metal coating systems. The results of this effort have been adequately summarized by Bartlett et al.[42], Jaffee[41], Harwood[173], and others[43, 115, 166, 245-247, 250]. The story of the extensive effort by the General Electric Co. to protect molybdenum turbine buckets, as related by Levinstein[43] and Downey, describes the long road between laboratory investigations and hardware in service; molybdenum turbine buckets are not yet a reality.

Figures 19 and 20 show some of the results obtained on nickel-chromium, nickel, and Inconel coatings.

Major shortcomings of Fe, Ni, Co-base coatings are: (1) large thermal-expansion mismatch which causes thermal fatigue in cyclic operation, (2) rapid inter-diffusion to form low-melting eutectics or brittle intermetallics, and (3) relatively low maximum use temperature.

Noble-Metal Base. Platinum, rhodium, and their alloys have been and are being considered as coatings for molybdenum. Shortcomings which have been found are (1) thermal-expansion mismatch, (2) interdiffusion during long-time exposure, and (3) suspected diffusion of oxygen through platinum to oxidize the molybdenum and cause rupture of the coating during long-time use.

Results reported by Rhys[248] for platinum-clad molybdenum, with and without an intermediate barrier layer, are given in Table 21.

TABLE 21. TIME TO FAILURE OF PLATINUM-CLAD MOLYBDENUM
SPECIMENS HEATED IN STILL AIR AT 2190 F (1200 C)[248]

Type	Life, hr	
	Maximum	Minimum
Unbonded, no intermediate layer	650	375
Bonded, gold intermediate layer	2,010	930
Unbonded, alumina intermediate layer	5,050	4,070

Diffusion of oxygen through platinum has been reported orally by others; it also has been reported orally that a platinum alloy prevents or greatly retards oxygen diffusion.
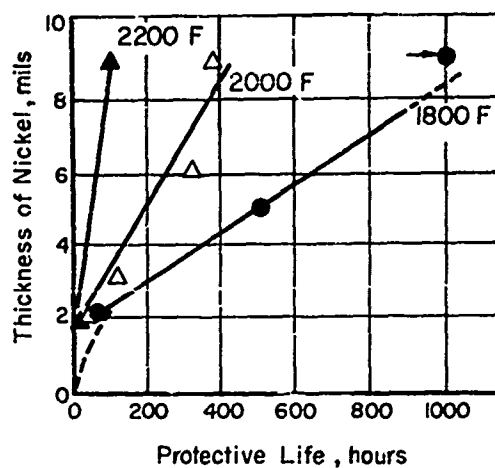
FIGURE 19. EFFECTIVENESS OF VARIOUS THICKNESSES OF NICKEL DEPOSITED ON 0.001 IN. OF CHROMIUM FOR PROTECTION OF MOLYBDENUM AGAINST OXIDATION AT 1800, 2000, AND 2200 F[245]
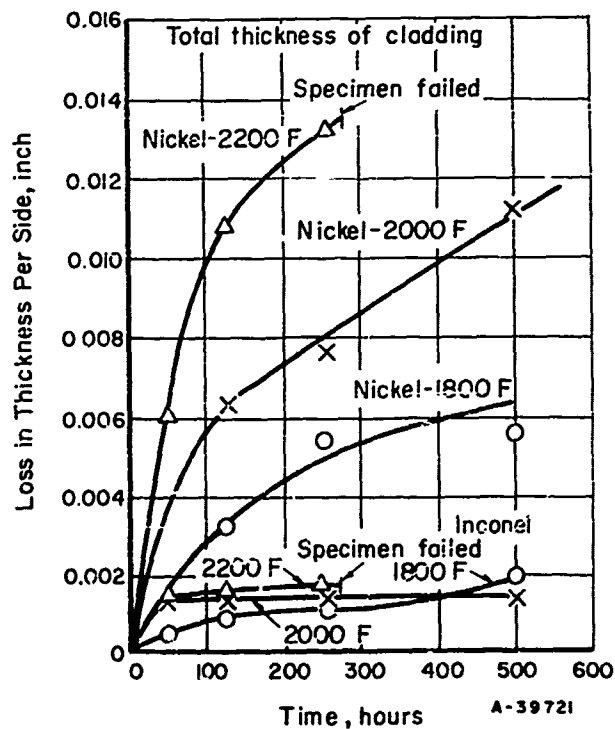
FIGURE 20. LOSS IN THICKNESS OF INCONEL-CLAD AND NICKEL-CLAD MOLYBDENUM IN AIR AT 1800, 2000, AND 2200 F (980, 1095, AND 1205 C) (UNSTRESSED CONDITION)[41]

Platinum and rhodium are being investigated currently for the high-temperature short-time applications involved in re-entry.

Miscellaneous-Metal Base. Coatings classified in this category are the chromium-base materials, chromium and Al-Cr-Si. The Al-Cr-Si compositions, although having a chromium base, might also be looked upon as intermetallic coatings. These coatings have appeared promising for different applications[42], and the sprayed Al_2O_3/chromium plate/Mo system is of appreciable current interest.

Chromium plate by itself has been found to be of limited value for the protection of molybdenum in a thermal-cyclic vibratory-stress environment at temperatures up to 2200 F.[251] Apparently the rapid embrittlement of chromium at service temperatures makes the plate highly susceptible to cracking under stress unless a restraining cover coat is applied.

The System 300 coating uses a 3 to 4 mil chromium plate overlaid with 8 to 10 mils of flame-sprayed alumina.[171,232] This coating has shown much promise in protecting molybdenum. It is relatively thick, and it cannot be applied to complex internal surfaces.

Chromium-nickel multilayered coatings have overcome some of the shortcomings of the chromium plate.[42] A report by Williams and Hammond[252] shows use of the benefits of both nickel and flame-sprayed Al_2O_3. Oxidation lives of 5-mil thick coatings ranged from 300 to 500 hours under conditions of limited daily cycling from about 2000 F. Measures to increase the chromium content of the outer zone of the diffused coatings were found to be effective in increasing the life and also appeared to improve reproducibility. A fourfold increase in life to 1200 hours was achieved by applying a 3-mil topcoat of sprayed alumina.

Silicide-Base Coatings of Advanced Status

It is well known that silicide-base coatings have been and continue to be under intensive research and development for solving several current protection problems with molybdenum. Table 19 shows that many organizations have been involved in this effort.

It is commonly held that vapor deposited silicide-base coatings on molybdenum via pack cementation offer the best potential for protecting molybdenum in several current and future space-vehicle applications.* Major effort on protective coatings today is directed toward satisfying the requirements of these applications. There are five coatings of this type which have attracted the most attention, viz., Disil, Durak-B, PFR-6, Vought II or IX, and W-2.

Disil.[226b,244b] In connection with the Dyna-Soar program, four coating processes have been developed at the Boeing Airplane Co. for the protection of molybdenum.

The Disil-1 coating is applied by pack-cementation siliconizing at about 1900 F using a glass-sealed retort containing silicon and iodine. The coating is essentially

*There is a fluidized-bed vapor deposition process under development at the Boeing Aircraft Co. However, the information released to date is too meager to be of value for making an assessment of the process or coating system produced therefrom.

MoSi$_2$. Ductility of the substrate is not appreciably altered by the process nor is the substrate measurably contaminated. However, the coated metal has less ductility than the bare metal.

The Disil-2 coating is applied by a hot dip in molten Al-12Si. Diffusion occurs in the hot-dip bath and excess aluminum is removed. Ductility and other substrate properties remain essentially unchanged.

Disil-3 is a modification of the Dis: . process. In Disil-3 the reacting iodine is int oduced into an evacuated reaction chamber ..t the coating temperature.

In the fluidized-bed process, volatilized iodine flows through a heated silicon bed containing the article to be coated.

It is believed that the Disil-1 process is developed to the greatest extent. Preliminary design data for Disil-1 coated Mo-0.5Ti are given in Table 22.

TABLE 22. PRELIMINARY DESIGN DATA FOR DISIL-1 COATED Mo-0.5Ti

Coating Thickness	0.9 mil/side
Coating Weight	0.01 lb/sq ft/side
Temperature Capability	Over 1 hour at 3000 F in moving air
Color	Black
Roughness	15-60 rms
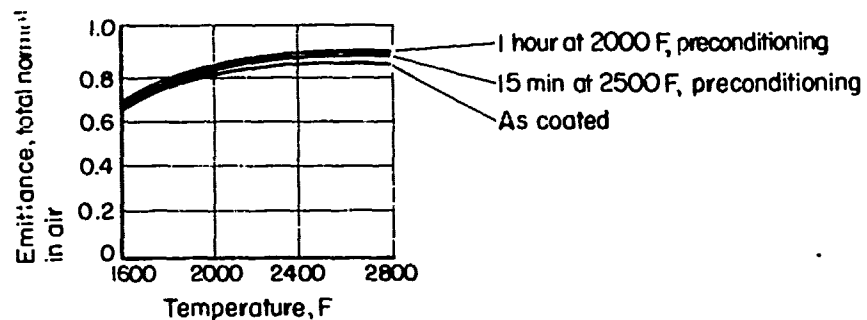
A-39762

Hardness	Very hard (off Rockwell scale)
Erosion Resistance	Good
Amount of Recrystallization Induced by Process	Negligible
Part Dimensional Changes	0 9-mil coating produces 0.75 mil growth/side
Minimum Coatable Hole Diameter	50 mils
Coating Thickness Control	±0.5 mil
Diffusion Stability	Good up to 2700 F
Self-Healing Properties	Good above 2500 F
Porosity	Not porous
Thermal-Shock Resistance	Good (1000 F/min heat-up, 200 F/min cool-down
Mechanical Properties	Tensile yield and ultimate, % elongation and Young's modulus being determined

Performance data for the Disil coatings have been reported as follows:

Coating Process	Coating Thickness, mils	Temperature, F	Protective Life, hr	Remarks
Disil-1	0.7, 0.9	2700	>0.5	No failure
	1.5	2700	5	No failure
	1.5	2700	15	Edge failure
	1.5	2700	<20	Substrate completely oxidized away
	2.1	2700	10	No failure
	0.9, 1.5	3000	1	No failure
	--	3200	Short times	--
Disil-2	--	3000	1/6, at least	--

Disil-3   Coatings comparable in oxidation resistance to Disil-1

Durak-B.[226c,253] This coating is the latest of a series of coatings developed by the Chromizing Corporation. It is a modified cementation-applied coating for use on molybdenum-base alloys.

Preliminary tests and initial experience have indicated that Durak-B is superior to earlier coatings in the Durak series with respect to reliability, reproducibility, service life, and tolerance for surface imperfections in the substrate.

The following performance and property data have been reported:

Oxidation Tests:

Temp, F	Life, hr

Slowly moving air, daily removal from Globar furnace for examination

2000	>7500, tests in progress
2400	225
2700	180

Oxygen atmosphere, 10 ft^3/hr

2880	Heating time 20 sec, no hold at temp, 22 cycles, no failure
2880	Heating time 3 min 33 sec, 1 hr hold, no failure
2880	Heating time 4 min 10 sec, 8 cycles

Electric resistance heating, air atmosphere

2500	10-minute heating and hold, 10 cycles, no apparent change

Temp, F	Life, hr

Gas-air combustion heating

2600	30-minute heating time, 30-minute hold, 30-minute cooling, 10 cycles, no failure

Thermal-Shock Tests:

2000	A Mo-0 5Ti cylinder, 2 inches in diameter x 1 inch long having 31-1/4-inch holes drilled parallel to 1-inch length and evenly spaced, was alternately heated to 2000 F (electrical resistance heating) and quenched in compressed air at 100 lb/sq in. to simulate a service condition. Earlier Durak types of coatings failed at 20 cycles. Durak-B survived 43 cycles without failure, and testing was terminated.

2500	Specimen resistance heated to 500 F and quenched with liquid oxygen to -325 F for r cycles. Same specimen was then heated to 2500 F and quenched with liquid oxygen to -325 F in less than 1 second for 5 cycles with no detectable change.

Emittance:

Temp, F	Spectral, 0.65 μ, argon
1700-2600	0.86
2960-3140	0.75

Temp, F	Total
1700	0.74
1880	0.75
2060	0.76
2240	0.77
2420	0.78
2600	0.78
>2600	0.94 (Aerojet)[226c]
2960-3140	0.95

The mode of failure of Durak-B has been reported to be general and time-temperature dependent, with no particular preference for edges and corners.

PFR-6. [222,226c] The PFR-6 coating, formed in single-cycle codeposition (Si + Cb) pack cementation, was developed by the Pfaudler Company. This coating was selected from several as the one which should be optimized. Under Air Force sponsorship, research is currently in progress to scale up the PFR-6 coating process and to optimize the coating performance by carrying out a statistically planned research program.

Table 23 gives the reported life of PFR-6 at several temperatures as determined by oxyacetylene torch testing. Preliminary data, shown in Figure 21, indicate that thicker coatings result in longer life at 3000 F.

TABLE 23. COATING LIFE OF PFR-6 AT SEVERAL TEMPERATURES[226c]

Temperature, F[a]	Coating Life, hr[b]
2800	12.5
2900	4.4
3000	--
3125	2.1
3230	0.5

(a) Estimated true temperature based on emissivity of 0.8.
(b) Average of three tests at each temperature using oxyacetylene torch.

Long oxidation tests at 1800 and 2000 F and cumulative oxidation testing at a series of elevated temperatures have been carried out by the Climax Molybdenum Company on PFR-6. The tests were carried out by heating each sample in a separate compartment in an electrically heated muffle furnace. Air was introduced at the rear of each compartment and was regulated to flow over the sample at a velocity of about 2½′ per min. During the test, samples were closely observed for evidence of failure indicated by evolution of molybdenum trioxide and were also inspected at intervals, at room temperature, for visible flaws. Data obtained at 1800 and 2000 F (Table 24) indicate that PFR-6 exhibits a life of approximately 1000 hours in this temperature range, although the reproducibility of the coating life could be improved. Within this test region, however, minimum life was 812 hours and maximum life at least 1000 hours.

TABLE 24. COATING LIFE OF PFR-6 AT 1800 F AND 2000 F[a,b][226a]

Sample	Total Hours at 1800 F	Total Hours at 2000 F	Remarks
1	500	500	OK
2	500	312	Failure at surface and edge
3	500	312	Complete failure
4	500	336	Failure at one end
5	500	356	Failure due to small blister
6	500	500	OK
7	500	428	Failure at surface
8	60	--	Coating was broken due to improper handling

(a) Data courtesy of Climax Molybdenum Company.
(b) Heating in electric muffle.
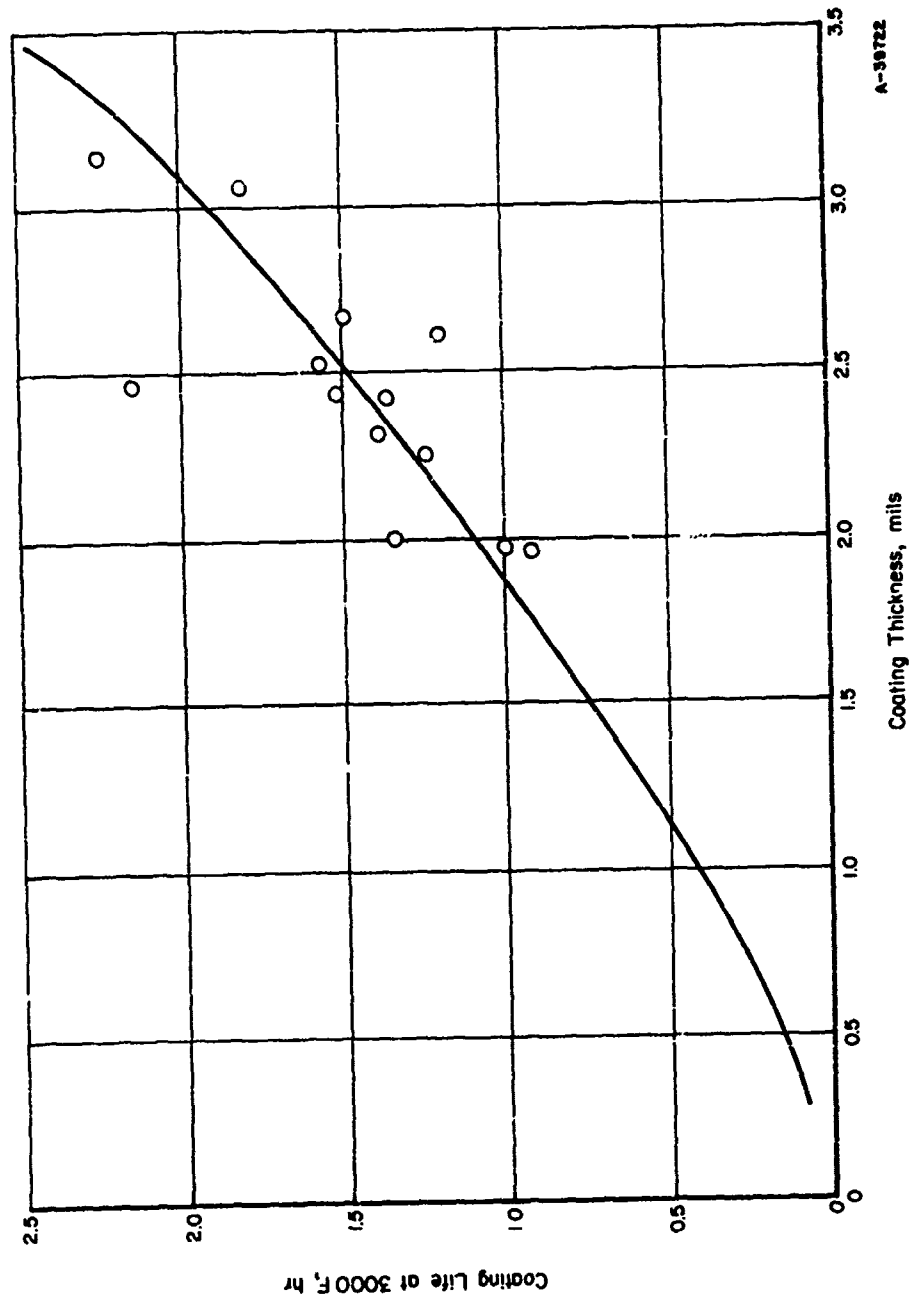
FIGURE 21. PFR-6 COATING LIFE VERSUS COATING THICKNESS(226 C)

The cumulative oxidation data (Table 25) indicate that FFR-6 protects Mo-0.5 per cent Ti substrate for time periods up to 25 hours within the temperature range 1800 to 2600 F. As much as 6 hours of this test exposure was at 2500 to 2600 F. The wide variations in coating life reported at elevated temperatures are probably associated with the range of test temperatures.

TABLE 25. CUMULATIVE OXIDATION TESTS OF PFR-6[a,b][226c]

Sample	Accumulated Coating Life, hours, at Indicated Temperature					
	1800 F	2000 F	2200 F	2400 F	2500-2600 F	2700-2900 F
9	8	4	4	4	5.5[c]	--
10	8	4	4	4	6.0	5[c]
11	8	4	4	4	5.5[c]	--
12	8	4	4	4	6.0	5[c]
13	8	4	4	4	4.0	Not completed
14	8	4	4	4	5.0	Not completed
15	8	4	4	4	5.0	Not completed
16	8	4	4	4	4.0	Not completed

(a) Data courtesy of Climax Molybdenum Company.
(b) Heating in electric muffle.
(c) Failed.

It should be pointed out that the data in Tables 24 and 25 were obtained with PFR-6 samples prepared in January, 1961. Since then the reproducibility of PFR-6 has been improved.

Thermal-shock tests on PFR-6 were also conducted by Climax. A specially constructed thermal-shock cycle apparatus was used in which the samples were heated from 80 F to testing temperatures in 30 seconds, held at testing temperature for 15 seconds, then cooled to 80 F in 45 seconds by air blast. Every 10 cycles the samples were allowed to cool in still air so that failures might be detected. Results are presented in Table 26.

Data obtained from low-temperature ductility tests (Table 27) indicate that the PFR-6 coating process does not severely impair the mechanical properties of the substrate.

In the Pfaudler Laboratory, oxidation tests were carried out on bent samples to determine the extent of damage brought about by bending. Samples were bent over a 1.5-in.-radius die at 150 F prior to the oxyacetylene torch test. Since in earlier, more severe bending tests failure appeared on the concave side of the bent samples, the torch flame was directed onto the concave side of the sample for the oxidation tests. As in previous work, the 3000 F test temperature was measured by an optical pyrometer assuming an emittance of 1.0. (Assuming an emittance of 0.8, the test temperature would be 3125 F.) In addition to the Climax test results, these postbend oxyacetylene torch test data (Table 28) indicate that the bend ductility of the PFR-6 coated Mo-0.5 per cent Ti substrate is adequate in the working range explored.

TABLE 26. THERMAL-SHOCK TESTS OF PFR-6 FROM 80 F TO TEST TEMPERATURE[a][226c]

Sample	Thermal-Shock Cycles		"1800 F Test", True Temp, F	Remarks
	End A[b]	End B		
17	500+	500+	1780-1810	OK
18	500+	500+	1780-1810	OK
19	500+	400	1780-1810	End B failed due to small blister
			"2000 F Test"; True Temp, F	
20	500+	500+	2000-2080	OK
21	500+	500+	2000-2080	OK
22	271	500+	2000-2065	End A failed with evolution of McO_3

(a) Data courtesy of Climax Molybdenum Company.
(b) The two ends of each specimen, designated A and B, were tested simultaneously.

TABLE 27. BEND DUCTILITY TEST OF PFR-6 COATED Mo-0.5 PER CENT Ti AT LOW TEMPERATURES[a][226c]

Condition of Sample[b]	Temperature, F	Bend Angle, degrees	Remarks
Uncoated	-80	7	Failed
Mo-0.5% Ti	-70	6	Failed
	-60	45	Failed
	-20	150	Limit of fixture[c]
	30	150	Limit of fixture[c]
	78	150	Limit of fixture[c]
As coated	78	8	Failed
	110	20	Failed
	120	16	Failed
	125	35	Failed
	130	150	Limit of fixture[c]
	150	150	Limit of fixture[c]
Coated samples exposed for 500 hr at 1800 F plus 25 hr at 2000 F	78	4	Failed
	150	3	Failed
	175	75	Failed
	200	150	Limit of fixture[c]

(a) Data courtesy of Climax Molybdenum Company.
(b) 30-mil-thick substrate.
(c) No failure.

TABLE 28. POSTBEND LIFE OF PFR-6 IN THE
OXYACETYLENE TORCH[226c]

Batch	Postbend Coating Life at 3000 F, hr[a,b]
1	1.53
	1.48
	1.95
2	1.47
	1.57
	1.38
3	1.68
	1.85
	1.98
4	1.82
	1.57
	1.80
5	1.42
	1.98

(a) 3000 F assuming emittance of 1.0 (3125 F assuming emittance of
0.8). Sample thermal shocked with 30 psi air blast every 0.5 hr.

(b) Oxyacetylene torch heating.

Vought II or IX.[226b,257] These coatings have been developed at the Chance
Vought Corporation. It is not known which coating currently is the most promising.
Figure 22 shows weight losses measured for these coatings on Mo-0.5Ti at 2800 F for
3.5 hours; presumably the coating systems were not run to failure. A life of 8 hours
at 2800 F in static oxidation has been reported for a 16-mil sheet specimen of Mo-
0.5Ti with a 1.2-mil coating.
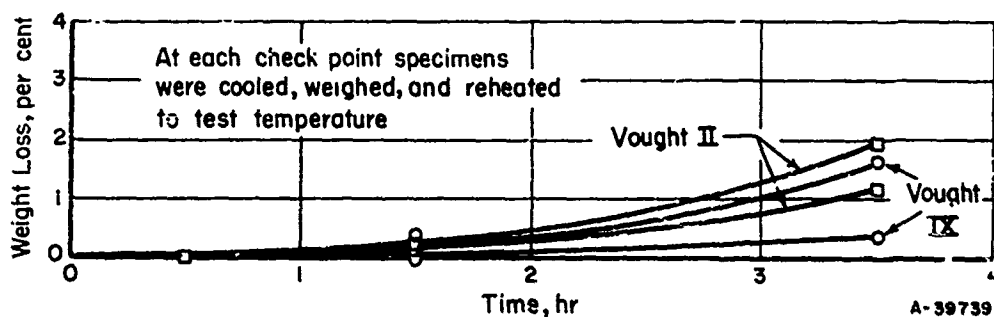
FIGURE 22. STATIC OXIDATION TESTS ON VOUGHT COATINGS FOR
Mo-0.5Ti AT 2800 F FOR 3.5 HOURS

Sustained-load thermal-cycling test results for Vought-coated Mo-0.5Ti have been reported as follows:

Load, per cent of ultimate tensile strength	Time, min			Temperature, F	Number of Cycles	Remarks
	Heating	At Temp	Cooling			
60	5	5	10	80-2000	40	No failure
60	5	5	10	80-2800	4	No failure

Table 29 gives results for repeated load tests; Table 30 gives room-temperature tensile properties of uncoated and coated Mo-0.5Ti; and Table 31 gives tensile-elongation data.

The reduction in tensile strength of coated Mo-0.5Ti (Table 30) has been reported to be directly proportional to the amount of substrate "removed" during coating (i.e., to the coating penetration depth). The coating does not seem to affect the substrate adversely otherwise. This conclusion is reported to hold for metal thicknesses as small as 10 mils.

__W-2.__ [22,221,226c] The W-2 coating was developed several years ago by the Chromalloy Corporation. As a result, this coating has been evaluated more extensively and by more different organizations than any other known coating for the protection of the refractory metals.

Optimization of the W-2 coating has been in progress under Air Force sponsorship for the purpose of establishing reliability and reproducibility. [221,226c] The program was planned, executed, and analyzed by statistical procedures. Reference should be made to the final report on this program for a full review of the objectives, procedures, and results. [221]

One conclusion reached in the program was that properly rounded sheet edges are a necessity if W-2 coated molybdenum is not to fail prematurely. It was found that failures on edges were randomly distributed among oxidation test data. Because edge preparation was not included as a variable in the study, and these failures were premature, analysis of the results was made with and without edge-failure data.

Part of the optimization program involved predicting the life of the optimum coating, and specifying the tolerance limits for these predictions. The predictions made are affected by whether edge failures are or are not included in the data. Edge failures influenced the average lives of the coatings and the shape of the distribution curve for the oxidation-test data. With edge failures included, the distribution curve tended to assume an extreme-value configuration. Without edge-failure data, the distribution curve had the normal symmetrical shape. The effects of edge failures can be seen from the predictions listed in Table 32.

TABLE 29. REPEATED LOAD TESTS ON VOUGHT COATED Mo-0.5Ti[226b]

Type of Specification	Type of Test	Surface Condition	Sheet Gage, in.	Stress of Load Limits for Cycling	Number of Cycles to Failure	Remarks
Tensile (A)	Tensile	Uncoated	0.0159	+8,500 to +82,500 psi	420,000	Failed in loading end
Tensile (A)	Tensile	Coated	0.0165	+6,900 to +67,000 psi	503,000	Failed in test section
Tensile (C)	Tensile	Coated	0.0173	+6,100 to +55,000 psi	2,018,000	No failure
Tensile (C)	Tensile	Coated	0.0168	+6,100 to +55,000 psi	1,000,000	No failure[a]
Rivet (B)	Tensile	Coated	0.016	+37.5 to +372.5 lb	204,000	Net tensile failure at holes
Rivet (B)	Tensile	Coated	0.016	+37.5 to +372.5 lb	87,000	40,000-60,000- 80,000[b]
Bend (E)	Bend	Coated	0.063	+40,000 to +40,000 psi	1,000,000	No failure[a]
Bend (E)	Bend	Coated	0.063	-40,000 to +40,000 psi	1,191,000	No failure[a]
Bend (E)	Bend	Coated	0.063	+50,400 to +50,400 psi	382,000	Failure

(a) Specimen was heated to 1600 F and held for 5 minutes after removal from test jig.
(b) Specimen was held 5 minutes at 1600 F after each of the cycles shown.

TABLE 30. ROOM TEMPERATURE TENSILE PROPERTIES OF UNCOATED
AND VOUGHT COATED Mo-0.5Ti[226b]

Gage, in.	Surface Condition	Test Temperature, F	Yield Strength, 1000 psi	Ultimate Strength, 1000 psi	Elongation, %
0.016	Uncoated	78	122.0	135.4	9.6
0.016	Coated	78	103.5	113.3	9.6

TABLE 31. TENSILE-ELONGATION STUDIES OF VOUGHT COATED Mo-0.5Ti[226b]

Gage, in.	Test Temperature, F	Maximum Stress, 1000 psi	Elongation of Coating, %	Remarks
0.016	78	110.0	1.5-2.0	No oxidation occurred on elongated area upon subjection to a static oxidation test
0.010	1600	18.8	2-3	
0.016	2800	14.3	14-15	

TABLE 32. PREDICTIONS OF MINIMUM LIVES OF THE OPTIMIZED
W-2 COATING BASED ON EXTREME-VALUE AND
NORMAL DISTRIBUTIONS[226c]

Edges	Tolerance Limit	Minimum Life at 2700 F, cycles[a]	
		Extreme-Value Distribution	Normal Distribution
Included	99.9	2.1	10.1
	99.0	9.8	13.4
	95.0	15.4	16.3
Excluded	99.9	6.4	13.0
	99.0	12.7	15.7
	95.0	17.3	18.1

(a) One cycle involves 2 hours at 2700 F, using furnace heating.

Because of the extensive evaluations which have been made on W-2 coated molyb-
denum, it is impractical and outside the scope of this report to review all of the avail-
able information. References to much of this information are as follows:

Category of Information	References
Oxidation	
Furnace	42,226b,235
Oxyacetylene torch	226b
Plasma torch	196,233,226b,237
Induction	232,234
Thermal Shock	42,171
Impact	171
Emittance	145,232
Mechanical Properties	
Bend	42
Compression	235
Creep	235,259
Flexure and fatigue	171,231
Stress rupture	42
Tension	42,231,232,234,235,260
Torsion	235
Hardware	
Corrugated core sandwich	234
GE-McDonnell test box	211,226b
Missile probes	258
Outer-wall heat shield	226c
Wedges	226b,235-VII

Figure 23 shows the relationship between W-2 coating thickness and life of
coated alloy sheet in cyclic furnace oxidation at 2700 F. The life of W-2 coated molyb-
denum sheet is shown as a function of temperature in Figure 24; it should be stated that
these data were reported in October, 1960, before the W-2 coating was optimized.
This statement holds also for most of the test results in existence at the time this re-
port was prepared.

Variation of tensile ultimate and yield stress, elongation, and Young's modulus
for W-2 coated Mo-0.5Ti tested in air is given in Figures 25, 26, and 27, respectively.
All of these tests, which were reported by Mathauser et al.[234], were performed at a
nominal strain rate of 0.005 inch per minute up to the yield stress and at an increased
rate of approximately 0.05 inch per minute above the yield stress. In the elevated-
temperature tests, the specimens were heated to the desired test temperature and ex-
posed to air at temperature for 0.1 hour prior to loading.

Information from various sources on normal total emittance versus temperature,
normal spectral emittance versus wavelength, and variation of normal spectral emit-
tance versus wavelength with heating time in air have been summarized in DMIC
Memorandum 103.[145] Although there have been serious discrepancies in emittance
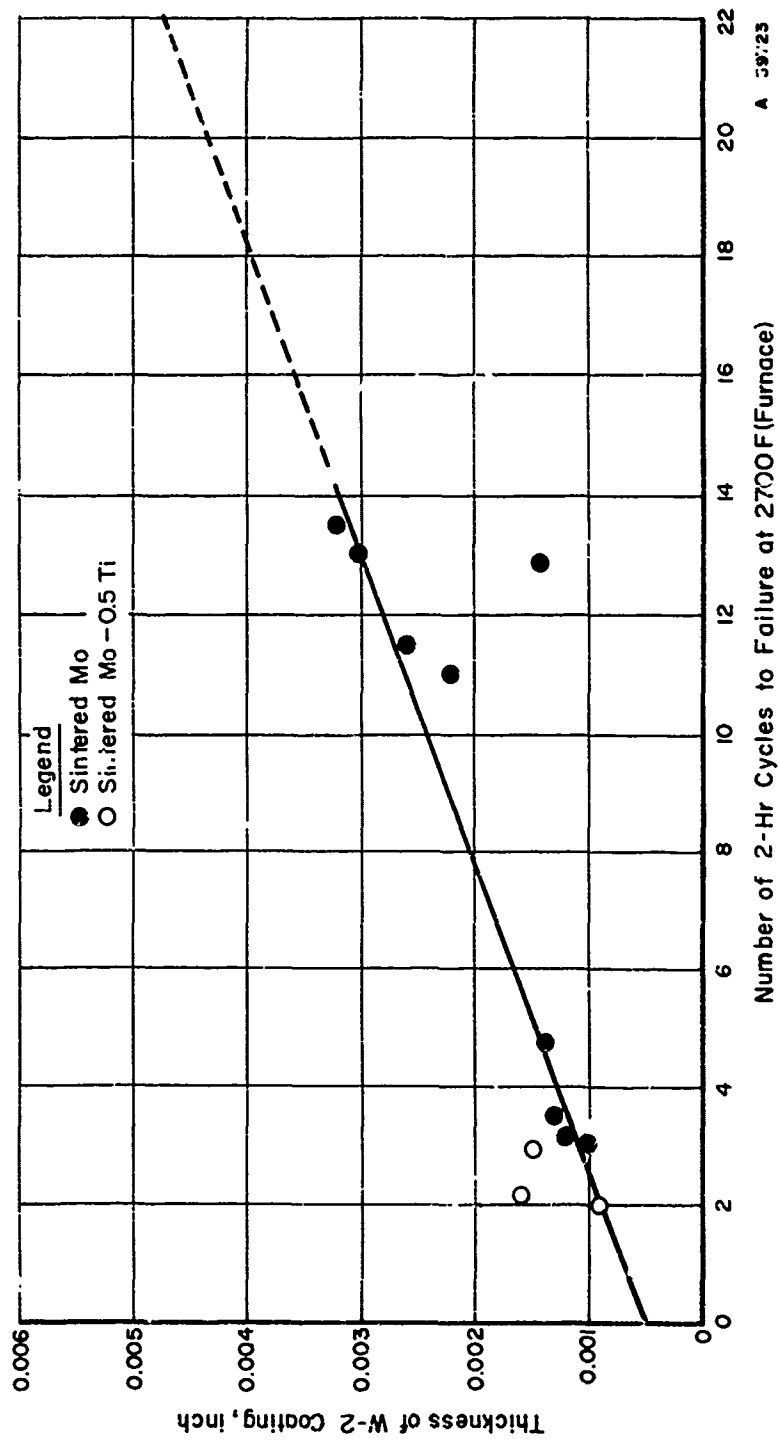
FIGURE 23. RELATIONSHIP OF W-2 COATING THICKNESS TO CYCLIC OXIDATION LIFE AT 2700 F[(22)]
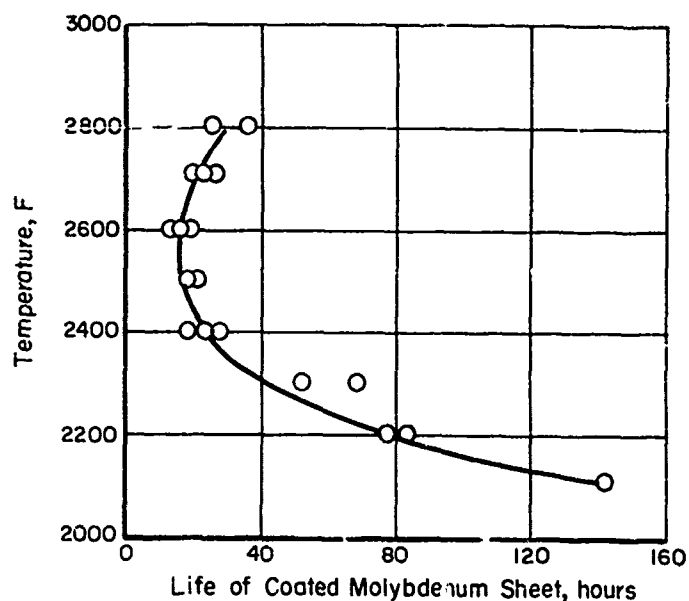
FIGURE 24. LIFE OF W-2 COATED OXIDATION SPECIMENS TESTED
IN AIR IN FURNACE[234]

Thickness of W-2 coating, 0.002 inch.
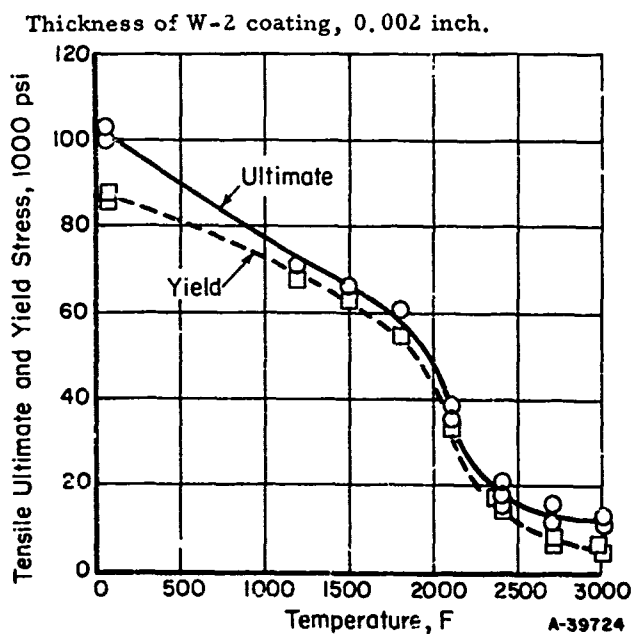
FIGURE 25. VARIATION OF ULTIMATE TENSILE STRESS AND 0.2 PER CENT
OFFSET TENSILE YIELD STRESS WITH TEMPERATURE FOR
W-2 COATED Mo-0.5Ti REPROCESSED SHEET[234]
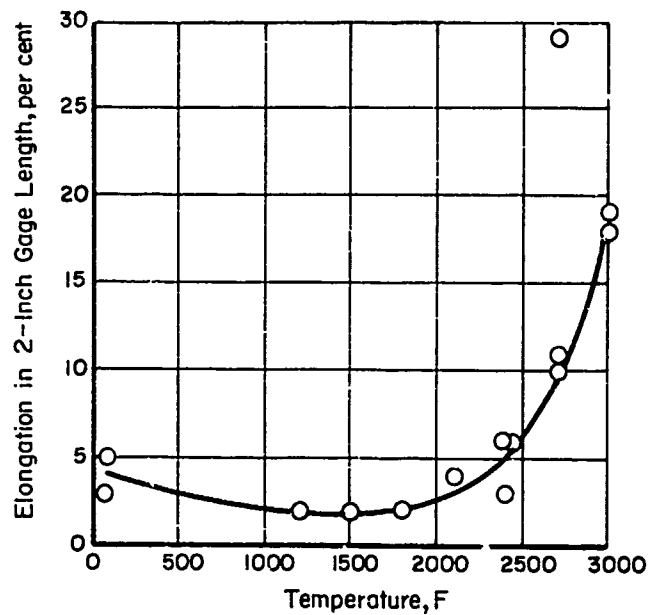
FIGURE 26. VARIATION OF PER CENT ELONGATION IN 2-INCH GAGE LENGTH WITH TEMPERATURE FOR W-2 COATED Mo-0.5Ti REPROCESSED SHEET[234]
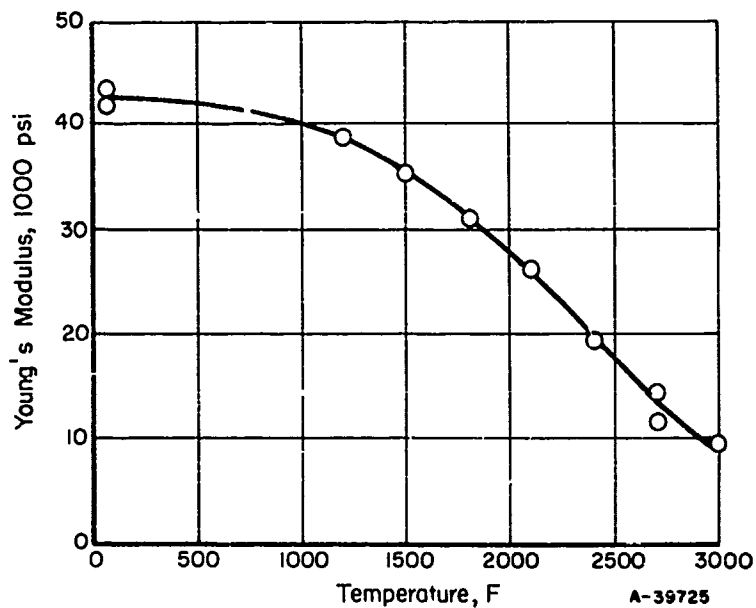
FIGURE 27. VARIATION OF YOUNG'S MODULUS WITH TEMPERATURE FOR W-2 COATED Mo-0.5Ti REPROCESSED SHEET[234]

data produced from different sources for the W-2 coating, probably due to, in part at least, the several factors discussed earlier under Emittance, it now appears that 0.6 is about the best value for the normal total emittance.

Coatings With Other Base Classifications and Unclassifiable Coatings

Information for three electrophoretic-type-coating efforts and one pack-cementation diffusion-coating effort is presented briefly in this section.

The Vitro coating of $MoSi_2$-6Ni applied to molybdenum by electrophoretic deposition and subsequent treatment (Tables 19 and 20, and Reference 180) has been reported to give protection for 100 hours at 2600 F and for 20 hours at 2700 F. This coating system has been reported to be in the research status. The Narmco and Thiokol coatings, which are applied by other methods, appear to have a somewhat similar over-all chemistry, but the reported upper use temperatures appear to be appreciably lower than that reported for the Vitro coating. These coatings have been classified as silicide-base coatings in Tables 19 and 20.

In two programs, recently sponsored by the Air Force, studies have been made on cermet-type coatings applied by electrodeposition techniques involving simultaneous electroplating and electrophoretic processes.

In the Value Engineering Co. program primary emphasis was on short-time erosion resistance and secondary emphasis on oxidation resistance directed toward rocket-nozzle applications. Data reported by Huminik[185] on coatings for molybdenum are presented in Table 33 (also reported were coatings for tantalum and tungsten, these will be presented in later sections).

Oxidation data on cermet electroplated coatings of $Ni-SiO_2$, $Cr-ZrO_2$, and $Ni-ZrO_2$ on molybdenum, as reported by Withers[183,226c], are given in Table 20. Depending on the metal-ceramic system, 5-mil coatings on molybdenum resisted oxidation at 2500 F for 2 to 5 hours in furnace heating with slowly moving air. These coatings have not been tested extensively, but, according to Withers[226c], they appear to offer potential in coating applications. The amount of ceramic can be controlled and graded from a very small amount to almost pure ceramic. This ability should be advantageous in matching the thermal expansion of a substrate, in accommodating mismatch by proper gradation, and in applying a virtually pure ceramic material on a graded cermet.

In addition to the work on cermet-type coatings, the American Machine and Foundry Co. very recently reported development work on diffusion coatings applied by pack-cementation techniques and designated as Amfkotes. According to Withers[226c], these coatings, which are applied in 5 to 20 hours in the temperature range of 1500 to 2200 F, are composed of various combinations of elements including Be, B, C, Mg, Al, Si, Ti, V, Cr, Fe, Ni, Zn, Zr, Cb, Mo, Ta, W, and Re. The following evaluation results were reported for Amfkote-2, which apparently is the most promising of the series for molybdenum.

TABLE 33. CHROMIUM-ZIRCONIUM OXIDE AND CHROMIUM-ZIRCONIUM
BORIDE COATINGS FOR MOLYBDENUM[185]

Specimen	Coating Thickness, mils	Time to Failure in Flame Test[a], seconds	Oxidation Screening[b], 1 hr at 2000 F	Thermal Shock[c]
Chromium-Zirconium Oxide				
K	3.15	380	No failure	No failure
L	3.25	390	Ditto	Ditto
M	3.15	350	"	"
N	4.95	495	"	"
Chromium-Zirconium Boride				
A	3.15	1500+	No failure	No failure
B	3.30	1845+	Ditto	Ditto
C	3.63	2000+	"	"
D	4.95	2500+	Pinhole oxidation	"

(a) Conducted on specimens 0.062 inch thick x 0.5 inch wide x 2.5 inches long. Specimen temperature maintained at 3860 F. Corrections for emittance and heat loss were considered in reported temperature. Flame chemistry was oxidizing.
(b) Electric-furnace heating.
(c) Test consisted of cooling specimen to 0 F and then submitting it immediately to the flame test until specimen was uniformly heated to 3860 F. This was followed by an immediate quench in cold water. Considered to be more severe test than actual rocket firing.

Temperature, F	Oxidation Life, hr	Heating Method
2800	19-45	Furnace
3000	8-9	Oxidizing flame
3200	8	Ditto
4200	3/4	"

Cyclic-oxidation resistance for greater than ten cycles was reported to be good and self-healing was indicated above 2300 F. Normal total emittance was reported as 0.76 at 750 F, 0.9 at 1139 F, and greater than 0.95 at 1337 F.

The life of Amfkote-3 coated molybdenum was reported as 264 hours at 2500 F; resistance to thermal shock was indicated to be less for Amfkote-3 than for Amfkote-2.

Comparative-Evaluation Programs
on Coating Systems

Although the results presented in this section are somewhat out of date, they are included to indicate (1) general broad trends, (2) the types of programs which have been carried out, and (3) the necessity for the establishment of end-application categories and associated standard evaluation techniques for protective-coatings systems.

With respect to the information in this section, the following points should be borne in mind:

(1) Amfkote-2 has been announced only recently.

(2) Disil is new with respect to all but one of the evaluations presented.

(3) Durak-B has supplemented or superseded the Durak MG coating.

(4) PFR-6 is new with respect to all but one of the evaluations, and has not been fully optimized as yet.

(5) Vought II or IX is new to all but one of the evaluations.

(6) W-2 has been optimized recently, and, with the possible exception of one evaluation, the optimized W-2 was not available.

Programs Oriented Toward Aircraft Gas Turbines.[171,236,249] The first major effort to protect refractory metals from oxidation was directed toward molybdenum for use in aircraft gas turbines. This application was of major interest until space applications became important. At the present time, the protection of turbine buckets in jet engines, although it remains unsolved, apparently has been relegated to a position of secondary importance relative to the space-vehicle application.

Doane[249], of the Climax Molybdenum Company, reported evaluations of the ductility and relative resistance to oxidation, thermal cycling, ballistic impact, and erosion of unalloyed molybdenum and Mo-0.5Ti coated with the following materials:

(1) Al-Cr-Si sprayed-metal coating

(2) Ni-Cr-B sprayed-metal coating

(3) Ni-Si-B sprayed-metal coating

(4) Composite coating of (1) and (3)

(5) Electroplated chromium

(6) Electroplated Cr-Ni composite

(7) Nickel cladding.

The evaluation tests were conducted at 1800 F.   Other tests included determination of ambient-temperature ductility of coated molybdenum and oxidation tests at temperatures up to 3000 F.   The behavior and nature of the general types of coatings studied were summarized as follows:

(1) <u>Al-bonded coatings</u>.   These coatings were characterized by excellent bonding to base molybdenum through the formation of a Mo_3Al-type layer which delayed oxidation of the underlying molybdenum.   In evaluation tests at 1800 F, the coatings exhibited good resistance to oxidation and thermal shock; moderate resistance to erosion; and poor resistance to ballistic impact.   Oxidation tests at higher temperatures indicated the coatings to be useful at temperatures up to 2600 F.

(2) <u>Ni-base coatings</u>.   These ductile coatings served well until cracks occurred, allowing oxidation through the cracks and resulting in the formation of nickel molybdate, which in turn accelerated failure under thermal cycling conditions.   In evaluation tests at 1800 F, the coatings exhibited good resistance to oxidation and ballistic impact; and moderate resistance to erosion and thermal shock.   Oxidation tests at higher temperatures indicated the coatings to be useful at temperatures up to 2200 F.

(3) <u>Cr and Cr-Ni electrodeposited coatings</u>.   Cracking of chromium promoted pit-type attack on underlying molybdenum.   The presence of a nickel overlayer delayed this attack.   In tests at 1800 F, these coatings exhibited good resistance to ballistic impact and erosion, erratic behavior in the oxidation test, and poor resistance to thermal shock.

It was stated that no one coating provided optimum protection under all evaluation-test conditions, and it was considered probable that individual uses for molybdenum would require coatings which emphasize one attribute in preference to others.

Giancola[236], of the WADD Materials Laboratory, reported an evaluation of protective coatings for molybdenum nozzle guide vanes.   Thirty-seven vanes were coated by 11 different organizations (only three were identified) for resistance to jet-engine operating conditions.   These vanes were evaluated in an engine exhaust stream at 1860 to 1890 F for a total time of about 4 hours.   The total time was broken down as follows: three periods of 1 hr each (to evaluate coatings for resistance to oxidation and erosion),

followed by three 15-minute and five 2-minute thermal shock cycles. The test program led to the following conclusions:

(1) Failure of electrodeposited metallic coatings occurred without exception on the inside coating or at the edges of the guide vanes.

(2) The outside coating of electrodeposited metallic coatings provided the best protection against oxidation and erosion of all the coatings tested.

(3) Metallic coatings, in general, withstood erosion better than the non-metallic aluminum-silicon-chromium dip and spray coating.

(4) Thinner coatings were less susceptible to thermal-shock cracking but suffered more through erosion leading to oxidation.

(5) All coating materials provided some degree of protection to molybdenum; however, no one coating gave complete protection throughout the 4-hour test period.

Mittenbergs et al.[231], of Battelle Memorial Institute, investigated the fatigue properties of coated molybdenum in tension-tension loading under various conditions of temperature and stress concentration. Three coatings were involved in the study:

(1) W-2

(2) Flame-sprayed Al-Cr-Si

(3) Nichrome-V-clad with a chromium diffusion barrier and with edges protected by weld beads.

Fatigue behavior was investigated and tensile properties were measured on unnotched and notched sheet specimens at 1800 F, ambient temperature, and -40 F. Testing of the coated specimens at 1800 F was done in air. Tables 34 through 37 partially summarize the information generated in this study. All coatings studied lowered the fatigue strength of unnotched and notched specimens at all three temperatures. The coatings increased the notch sensitivity in all cases. Thus, the coatings were more detrimental to the fatigue strength of notched specimens than to that of unnotched specimens.

In this program, the W-2 coating proved to be the most reliable of the three coatings investigated. The reliability of the Nichrome-V-clad molybdenum by itself proved to be very good. However, the protection of the edges presented a critical problem. Edge welds required considerable care and inspection. In addition, edge welds caused undesirable notch effects at room and low temperatures. The Al-Cr-Si coating had considerable variation and poor adherence, and its reliability was low.

TABLE 34. TENSILE PROPERTIES OF MOLYBDENUM SPECIMENS[231]

Average Data

Surface Condition	Ultimate Tensile Strength, 1000 psi	0.2 Per Cent Offset Yield Strength, 1000 psi	Elongation, per cent
		Room Temperature	
Unprotected	105.4	99.3	26.5
W-2 coated[a]	94.5	88.0	30.9
Al-Cr-Si coated[a]	89.5	80.0	31.2
Clad[b]	91.7/111.9	88.7/108.3	1.6
		1800 F	
Unprotected	51.6	44.2	9.0
W-2 coated[a]	45.7	42.2	11.8
Al-Cr-Si coated[a]	42.4	37.7	14.2
Clad[b]	39.6/48.3	35.6/43.4	14.0
		-40 F	
Unprotected	121.2	(c)	0.06[d]
W-2 coated[a]	84.9	(c)	0[d]
Al-Cr-Si coated[a]	119.4	(c)	0.10[d]
Clad[b]	56.3/68.6	(c)	0[d]

(a) Stress values are based on cross section before coating.

(b) Of the two stress values given, the first are based on specimen cross section, including the cladding, before edge welding, and the second refer to molybdenum only. The latter are 1.22 times higher, with the factor of 1.22 determined from average thickness measurements of layers in samples of clad material.

(c) Specimens failed before reaching 0.2 per cent offset yield point.

(d) Determined from stress-strain recordings.

TABLE 35. COMPARISON OF FATIGUE DATA OBTAINED AT 1800 F[231]

Surface Condition:	Unprotected	W-2 Coated[a]	Al-Cr-Si Coated[a]	Clad[b]
Ultimate Tensile Strength, 1000 psi	52	46	42	48
Elongation in Static Tests, per cent	9	12	14	14
Fatigue Strength (Maximum Stress) at 10^7 Cycles, 1000 psi				
Unnotched Specimens	28	26	23	26
Notched Specimens	26	15	14	18
Fatigue Notch Factor, K_f''	1.08	1.73	1.64	1.44
Fatigue Strength (Maximum Stress) of Unnotched Specimens at 10^7 Cycles, per cent of ultimate tensile strength	54	57	55	54
Fatigue Strength at 10^7 Cycles, per cent of unprotected samples at 10^7 cycles				
Unnotched Specimens	--	93	82	93
Notched Specimens	--	58	54	69

(a) Based on specimen cross section before coating.
(b) Based on cross section of the molybdenum core only.

TABLE 36. COMPARISON OF FATIGUE DATA OBTAINED AT ROOM TEMPERATURE[231]

Surface Condition:	Unprotected	W-2 Coated[a]	Al-Cr-Si Coated[a]	Clad[b]
Ultimate Tensile Strength, 1000 psi	105	94	89	112
Elongation in Static Tests, per cent	26	31	31	1.6
Endurance Limit (Maximum Stress), 1000 psi				
Unnotched Specimens	90	68	76	67
Notched Specimens	55	40	42	17
Fatigue Notch Factor, K_f''	1.64	1.70	1.81	3.94
Endurance Limit (Maximum Stress) of Unnotched Specimens, per cent of ultimate tensile strength	86	72	85	60
Endurance Limit, per cent of unprotected samples				
Unnotched Specimens	--	76	84	74
Notched Specimens	--	73	76	31

(a) Based on specimen cross section before coating.
(b) Based on cross section of the molybdenum core only.

TABLE 37. COMPARISON OF FATIGUE DATA OBTAINED AT -40 F[231]

Surface Condition	Unprotected	W-2 Coated[a]	Al-Cr-Si Coated[a]	Clad[b]
Ultimate Tensile Strength, 1000 psi	121	85	119	69
Elongation in Static Tests, per cent	0.06	0	0.10	0
Endurance Limit (Maximum Stress), 1000 psi				
Unnotched Specimens	127	80	98	74
Notched Specimens	78	40	49	43
Fatigue Notch Factor, K_f''	1.63	2.00	2.00	1.72
Endurance Limit (Maximum Stress) of Unnotched Specimens, per cent of ultimate tensile strength	105	94	82	107
Endurance Limit, per cent of unprotected samples				
Unnotched Specimens	--	63	77	58
Notched Specimens	--	51	63	55

(a) Based on specimen cross section before coating.
(b) Based on cross section of the molybdenum core only.

Graham and Hall[171], of the General Electric Co., FPLD, conducted an investigation of the following coatings on molybdenum at 2200 F by thermal shock, flexure (fatigue), and impact tests:

Manufacturer	Coating	Coating Material[a]	Process
Linde Air Products	LM-5	$MoSi_2$	Sprayed (detonation gun)
Climax Molybdenum	Al-Cr-Si	Al-Cr-Si	Flame sprayed and thermally diffused
Chromalloy Corp.	W-2	$MoSi_2$ + Cr	Pack reaction
General Electric Co.	System 300	Cr + Al_2O_3	Plating and flame spraying

(a) Coating material reported by Graham and Hall[171].

Thermal shock and flexure testing were conducted in the GE flame tunnel described in the referenced report. The buckets were thermal cycled from 1000 to 2200 to 1000 F, utilizing a 2-minute cycle. One bucket of each coating set was cycled until failure was observed. The other bucket of the same coating set was then thermal cycled 100 times, impacted, and then cycled until failure was observed.

A Krouse mechanical fatigue machine incorporating a variable displacement head was used to load the specimens for fatigue testing. The specimens were so loaded that there was an estimated outer fiber stress of 10,000 psi at 2200 F. The specimens were under observation during testing, and times of initial failure (observance of MoO_3 smoke) and complete failure (specimen broke) were noted and are indicated in Table 38.

A "BB"-type air gun which propelled a 1/16-inch stainless steel pellet at an impact velocity of 750 feet per second was used to impact test the specimens while they were being exposed at various temperatures within the flame tunnel. As summarized by Graham and Hall, "the relative order of merit, as based on these tests would be, beginning lowest, Linde LM-5, Climax Al-Cr-Si, Chromalloy W-2, and General Electric System 300 which had the highest order of merit."*

Programs Oriented Toward Space Vehicles. Comparative evaluation programs of coatings for molybdenum in space-vehicle applications have generated information on protective life as it is affected by temperature, reduced pressure, and strain, and on the tensile and compressive properties of coated molybdenum. The organizations who conducted these studies performed the evaluations, but in general, did not prepare the coated specimens.

The Martin Company.[232,266] The effects of temperature, pressure, and strain on the life of four coating systems was investigated by Wilks and Magalotti on a statistical basis using the following test conditions:

(1) Temperatures from 2000 F to the maximum at which the coatings afforded protection.

*See the remarks by Seelig and by Graham and Hall in the section of this report on Reliability.

TABLE 38. RESULTS OF THERMAL AND FLEXURE TESTS ON COMMERCIALLY COATED MOLYBDENUM SPECIMENS[171]

| Manufacturer | Turbine Buckets | | Flexure Specimens | | | | Flexure |
| | Specimen No. | Thermal Cycles to Failure[a] | Thermal Cycles to Failure[a] | | | | Oscillations[b], $\times 10^{-6}$ |
			Initial[c]	Dev.[d], %	Final[e]	Dev., %	
Linde-LM5	1	25	190	9.8	326	12.8	0.950
	2	25	156		252		0.721
Climax-Al-Cr-Si	1(f)	233	200	20	274	20	0.692
	2(f)	100 + 21	300		411		1.002
Chromalloy-W-2	1(f)	321	296	3.3	361	7.8	0.926
	2(f)	100 + 111	315		423		1.108
GE System 300	1(f)	938	814	1.5	1431	5	2.94
	2(f)	100 + 440	790		1294		2.4

(a) 1000 to 2200 F, 2-minute cycles.
(b) 10,000 psi (single amplitude), 24 cps.
(c) Observance of McO3 smoke.
(d) Per cent deviation from the average of the two tests.
(e) Specimen broke.
(f) 100 thermal shocks, then impacted at various temperatures, then thermal shocked to failure.

(2) Pressures from 0.01 to 1 atmosphere.

(3) Strains from 0 to 1 per cent.

(4) Time at temperature to 1-1/2-hr maximum.

The experimental test program was formulated on the assumption that two basic types of failure might be expected to occur in diffusion-type coatings: (1) cracking failures and (2) diffusion failures. Cracking failures are characterized by discrete separations in the coating, exposing the base metal to oxidation. This type of failure is primarily a function of temperature and strain. Diffusion failures, in contrast, are always time-dependent since, by definition, they occur as a result of gradual changes in the protective barrier as diffusion progresses.

The following four coatings on Mo-0.5Ti were evaluated:

(1) W-2 (Chromalloy Corp.)

(2) Al-Si (National Research Corp.)

(3) Al-Cr-Si (Climax Molybdenum Corp.)

(4) GE System 300 coating (General Electric Co.).

Three types of tests were conducted:

(1) Tensile tests, at both room and elevated temperature, to evaluate the strength and ductility of the coated material.

(2) Strain tests to determine the deformation which the coatings could tolerate before cracking.

(3) Oxidation tests to evaluate the effects of temperature, pressure, and strain on coating life. (Coating failure was signified by the appearance of the volatile MoO_3 oxide.)

The results of these studies are documented in a report[232] prepared for the U. S. Navy Bureau of Weapons.

The effect of temperature on tensile strength and ductility of coated Mo-0.5 per cent Ti alloy is shown in Figures 28 and 29. The coatings drastically reduced the room-temperature ductility of all samples. However, coated specimens did exhibit ductility in the temperature range of 500 to 3000 F, but these tests provide no measure of coating ductility as such. Strain-to-coating failure tests revealed the strains which could be tolerated before cracking occurred. These strains, in general, first increased gradually with temperature, then increased abruptly as shown by the data in Figures 30 through 34. Data obtained from the Al-Si and the Al-Cr-Si coatings suggested that they exhibit ductility at somewhat lower temperatures than the W-2 coating. However, differences observed in two lots of the same coating were as large, in some cases, as differences among the various coatings.
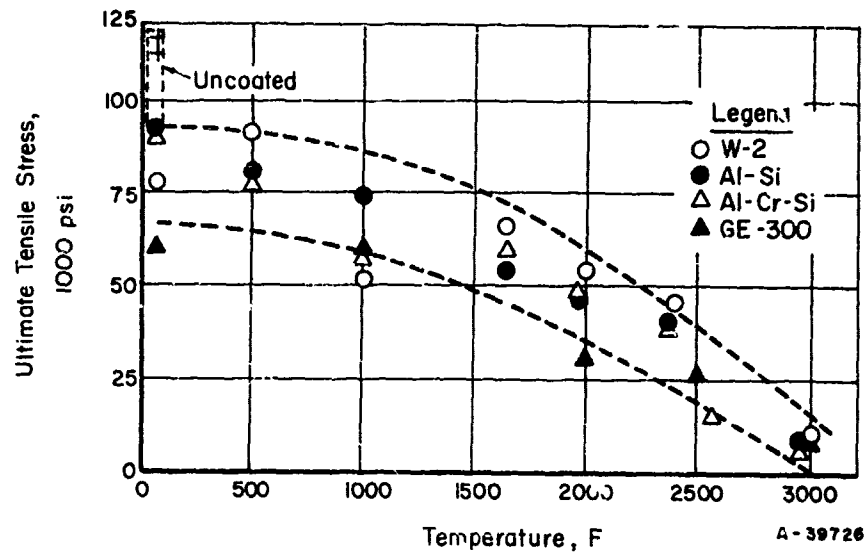
FIGURE 28. EFFECT OF TEMPERATURE ON TENSILE STRENGTH
OF COATED Mo-0.5 PER CENT Ti ALLOY[232]
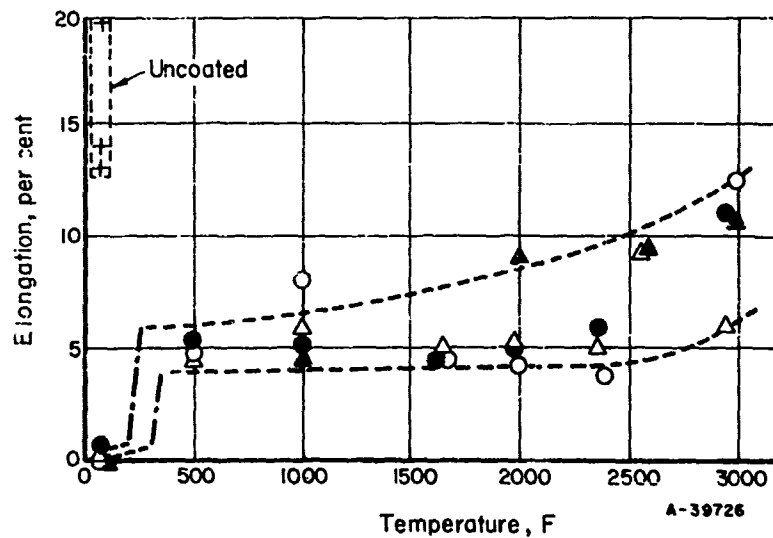
FIGURE 29. EFFECT OF TEMPERATURE ON TENSILE DUCTILITY OF COATED
Mo-0.5 PER CENT Ti ALLOY[232]
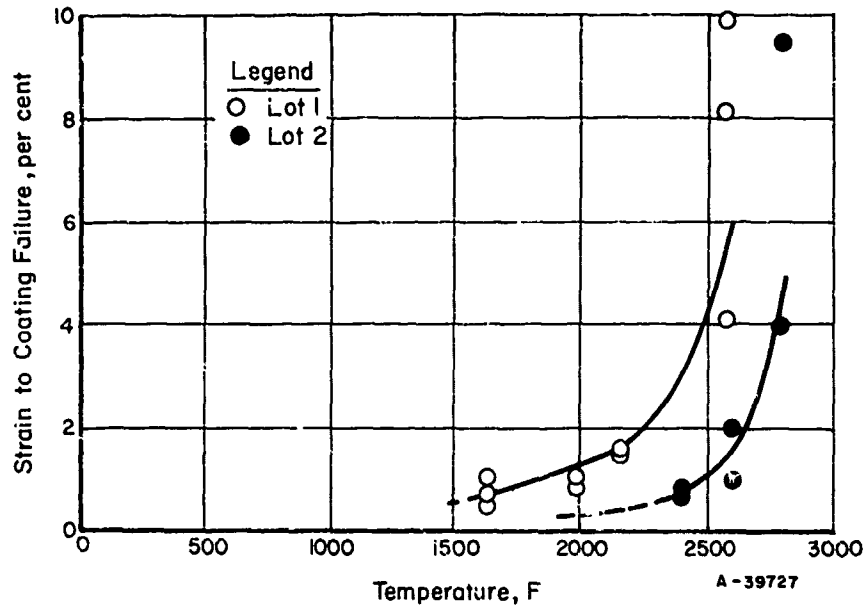
FIGURE 30. EFFECT OF TEMPERATURE ON STRAIN TO COATING FAILURE OF
W-2 COATED Mo-0.5 PER CENT Ti ALLOY[232]
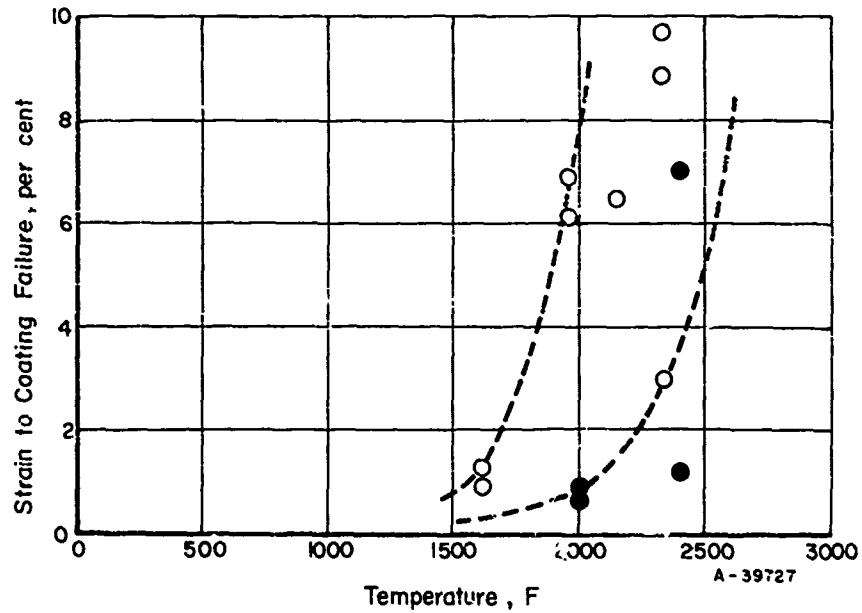
FIGURE 31. EFFECT OF TEMPERATURE ON STRAIN TO COATING FAILURE OF
Al-Si COATED Mo-0.5 PER CENT Ti ALLOY[232]
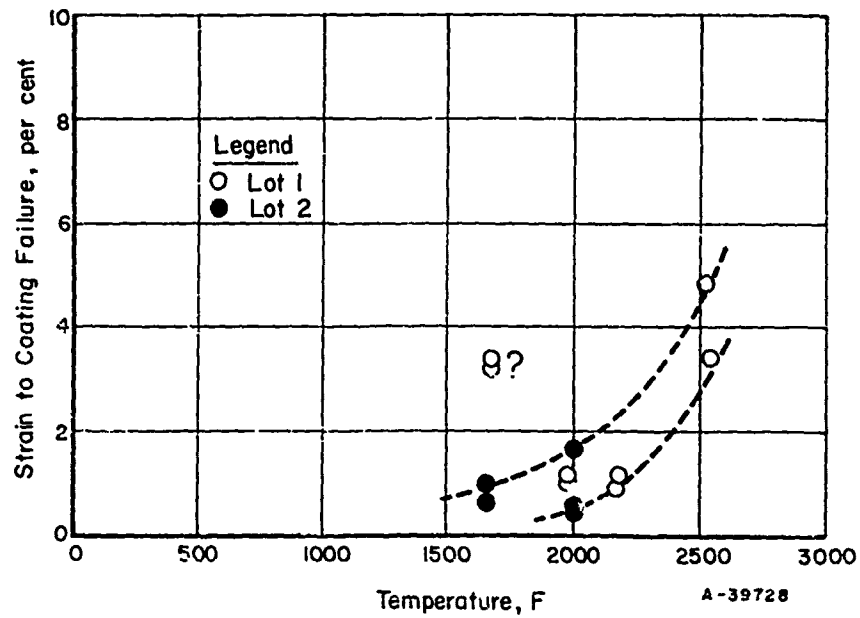
FIGURE 32. EFFECT OF TEMPERATURE ON STRAIN TO COATING FAILURE OF Al-Cr-Si COATED Mo-0.5 PER CENT Ti ALLOY[232]
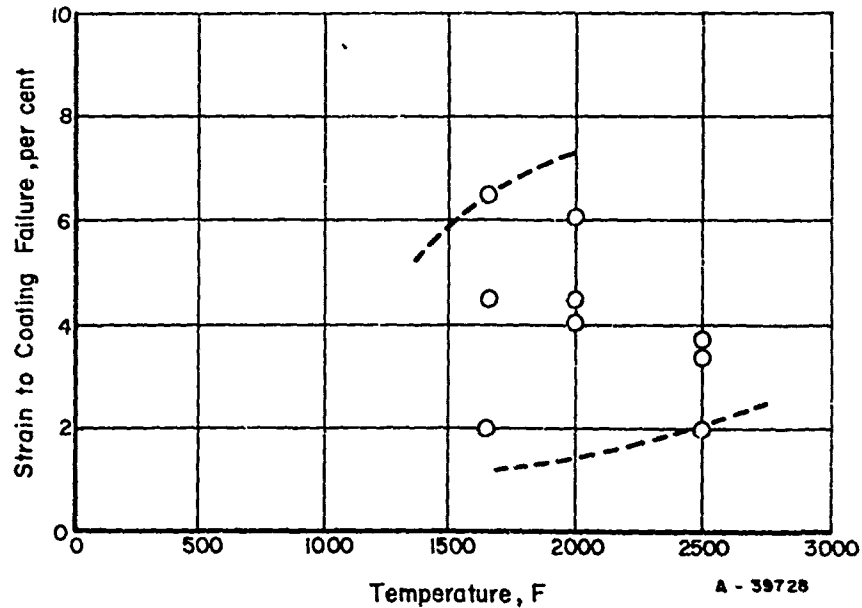
FIGURE 33. EFFECT OF TEMPERATURE ON STRAIN TO COATING FAILURE OF GE 300 COATED Mo-0.5 PER CENT Ti ALLOY[232]

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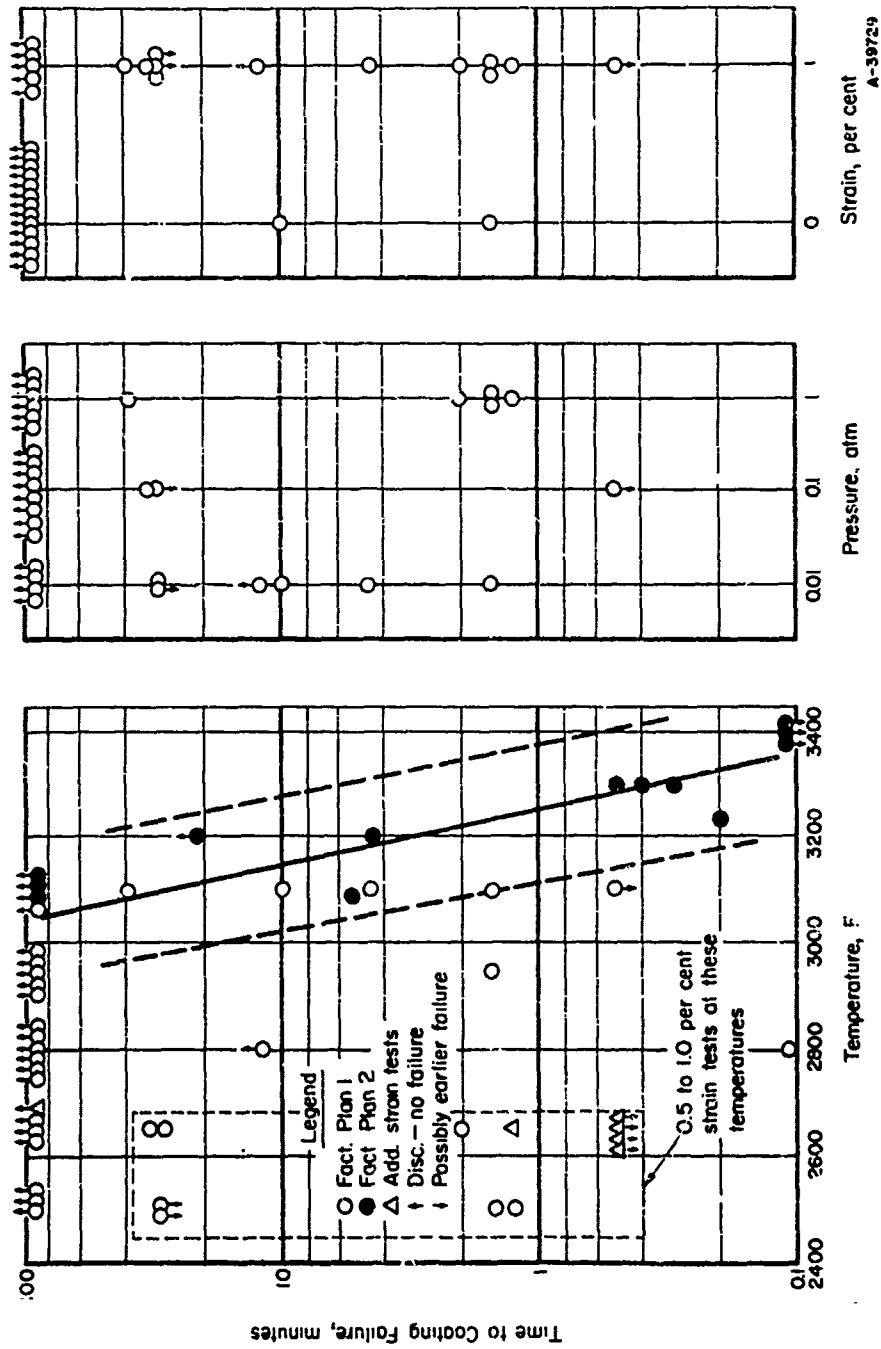
FIGURE 34. EFFECT OF TEMPERATURE, PRESSURE, AND STRAIN ON TIME TO COATING FAILURE OF W-2 COATED Mo-0.5 PER CENT Ti ALLOY(232)

For the W-2 coating, tested at temperatures below 3100 F, failures did not, in general, occur within the 90-minute maximum exposure time employed. Tests at higher temperatures, however, revealed that temperature is a highly significant factor in the time necessary for the coating to fail. The ambient pressure did not have any measurable effect on coating life. Strain levels below those which crack the coating had no measurable effect on coating performance. Over-all data for the W-2 coating suggested that strain at the 2500 to 2650 F temperature level should be limited to somewhat less than 0.5 per cent, while at 2800 F and above, strains can be tolerated to at least the 1 per cent level (Figure 34).

Tests on the Al-Si coating, conducted in the temperature range from 2500 to 3100 F, revealed that temperature is again the overriding factor influencing coating life (Figure 35). Pressure and strain did not grossly affect coating performance within the range studied. Tests conducted on the Al-Cr-Si coating, in the range of 2000 to 3100 F gave extremely erratic results due to variations in the coated specimens. Coating failure, as revealed by the formation of the volatile molybdenum trioxide, was observed during heating to the test temperatures in numerous specimens. The GE 300 coating is a duplex coating consisting of a 5-mil chromium plate and an additional flame-sprayed layer of aluminum oxide. Tests indicated that this coating has a limited but consistent coating life to temperatures up to 3000 F, but the coating life decreases rapidly thereafter. Pressure and strain to 1 per cent above 2800 F did not grossly affect coating performance (Figure 36).

In summary, it was concluded that the W-2 coating exhibited the best temperature capabilities with extended life to about 3000 F. The GE 300 coating had limited life at 3000 F, and the temperature capabilities of the Al-Si and Al-Cr-Si coatings were still further restricted The W-2 coating had less strain tolerance before cracking at 2500 to 2650 F than the other coatings, but exhibited adequate ductility at higher temperatures. All coatings were quite brittle at room temperature but exhibited ductility above 1600 F.

North American Aviation.[267] Simple test coupons of molybdenum TZM were submitted to three suppliers for application of their protective coatings. The coated coupons were then tested by: (1) a succession of 1-1/2-hour thermal cycles (each cycle including 1/2 hour at maximum temperatures up to about 3000 F, and (2) a continuous exposure to a high-velocity gas stream at temperatures up to about 3000 F. Based on the screening test results, cost, and availability, the Durak coating was selected for further testing. Two of the significant screening-test results were as follows:

Sample	Test	Temp, F	Results
TZM/Durak	Thermal cycle	2800	4 cycles with 1.6 per cent weight loss; edge and surface failure
TZM/Durak	Erosion	3000	1.5 hours with 0.05 per cent weight loss; edge failure only

WADD/The Pfaudler Company.[244b,226c] Coupons of coated Mo-0.5Ti (1.5 x 3 x 0.03 inch) were tested at The Pfaudler Company under the observation of Mr. J. R Myers, of the Dynasoar Engineering Office, WPAFB. The coupons .ere tested in
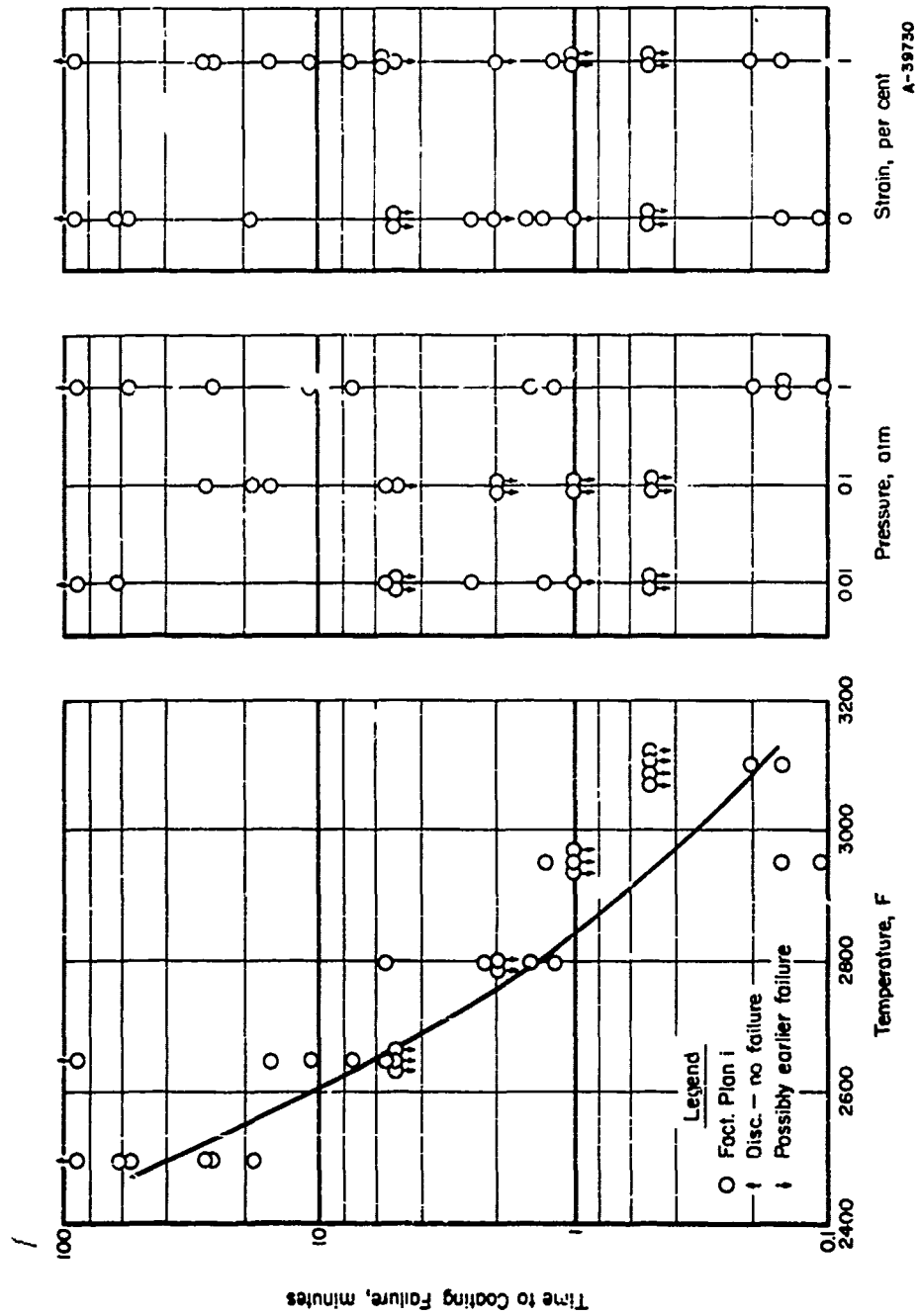
FIGURE 35. EFFECT OF TEMPERATURE, PRESSURE, AND STRAIN ON TIME TO COATING FAILURE OF Al-Si COATED Mo-0.5 PER CENT Ti ALLOY(232)
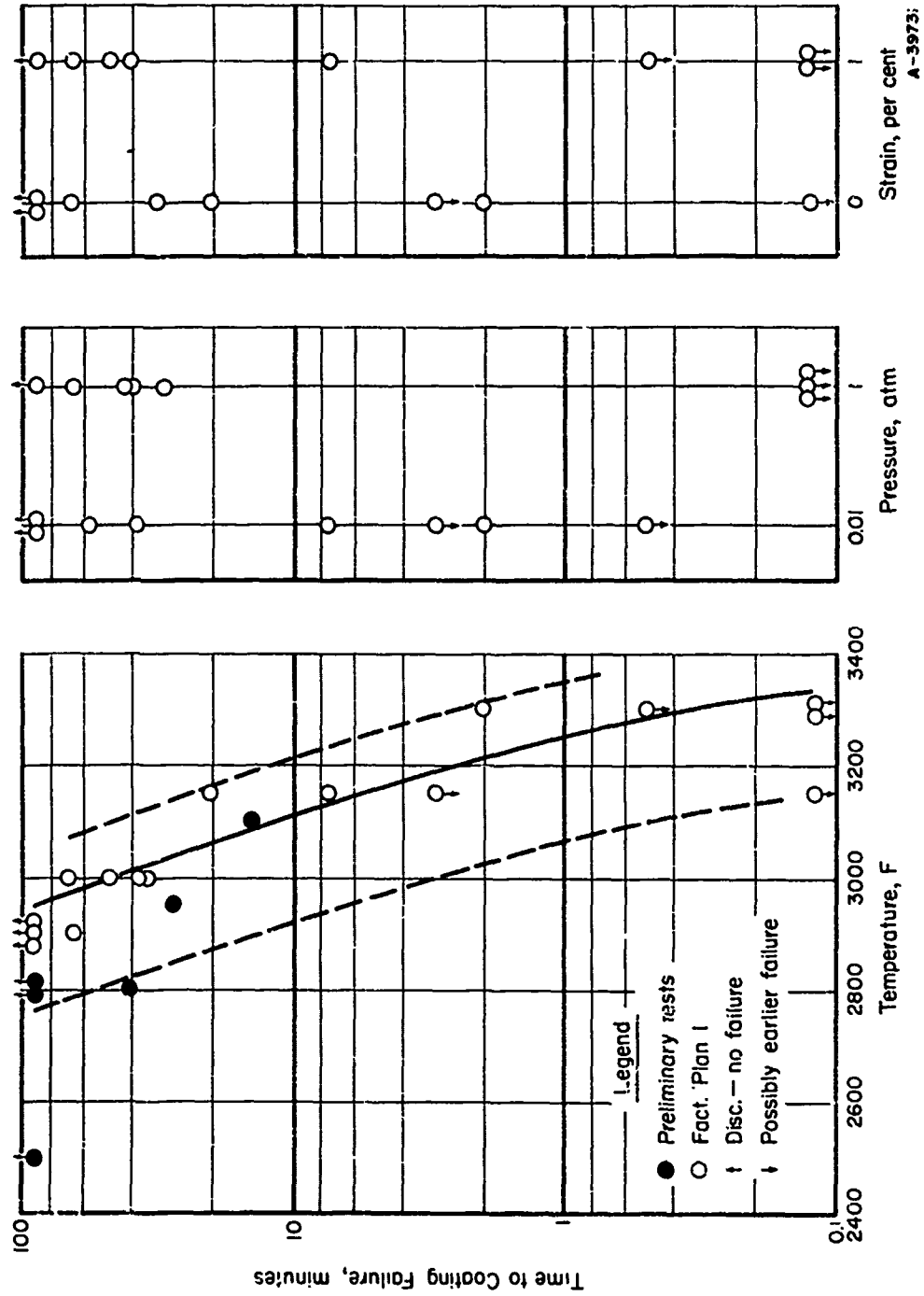
FIGURE 36. EFFECT OF TEMPERATURE, PRESSURE, AND STRAIN ON TIME TO COATING FAILURE OF GE 300 COATED Mo-0.5 PER CENT Ti ALLOY(232)

triplicate in Pfaudler's oxidizing oxyacetylene torch facility with cold-air blasts at
1/2-hour intervals. Additional procedural details of the experimental work beyond
these are not known. Results were as follows:

| Coating Designation | Coating Thickness, mils | Life at Indicated Temperature, hr | | | |
| | | Coupon | | Average | |
		2850 F	2960 F	2850 F	2960 F
Disil-1	1.5	1.00	0.47		
		1.23	0.50		
		1.30	0.58	1.18	0.52
PFR-6	2-2.5	2.13	1.07		
		2.38	1.10		
		3.12	1.37	2.54	1.18
Vought II or IX	3.5-4	3.42	1.00		
		3.77	1.12		
		4.15	1.40	3.78	1.17
W-2	2-2.5	(0.80)	0.35		
		1 68	0.40		
		1.72	0.42	1.40 (1.70)	0.39

Langley Field, NASA.[233,237] A number of leading-edge specimens of Mo-
0.5Ti, coated with Durak and W-2, were tested by Peters and Rasnick[233] in a 6-inch
subsonic low-pressure arc-powered tunnel and a 1,500-kw subsonic arc jet. The re-
sults indicated that these coatings provide adequate protection at temperatures up to
3000 F for the durations of the tests in these facilities, i.e., approximately 70 seconds
in the arc tunnel and approximately 10 minutes in the arc jet. Weight losses (<0.5 per
cent) experienced by a few of the coated specimens suggested that tests of longer dura-
tion in these environments may prove deleterious and that the stability of the coatings
might be reduced under the low-pressure environmental conditions encountered during
re-entry.

Trout[237] tested models of coated Mo-0.5Ti in a Mach 2.0 air jet at an average
stagnation temperature of about 3800 F and a stagnation pressure of 105 psia for ap-
proximately 60 seconds or until the model failed. Conclusions reached were as follows:

(1) Under the test conditions, models of Mo-0.5Ti were successfully pro-
tected against oxidation by chrome plate, Chromalloy W-2, nickel
aluminide, and flame-sprayed molybdenum disilicide.

(2) Models of Mo-0.5Ti coated with chrome-nickel plate, flame-sprayed
zirconia-molybdenum laminate, and flame-sprayed alumina-
molybdenum laminate failed during the test.

Picatinny Arsenal.[196] Experimental probes of molybdenum were prepared with
eight different coatings and subjected to varying heat inputs for a total duration of
60 seconds in a small, water-stabilized plasma arc. The initial heat input was

100 Btu's/(ft^2)(sec); the heat input was gradually i. re a... d to 500 Btu's/ ft^2)(ec) after 25 second:, then slowly decreas.d to 400 Btu's/(f: f's ec afte ... ...s. The temperatures attained on the leading-ed,: surfaces ʳur ʲtl t .ts were de.ermined with an optical pyror :ier.

Under these conditions of equal heat input, the sur ice temperatu es of the probes varied c..siderably due to the different emissivities, thermal conductivities, decomposition rates, and densities. A probe coated with zirconium diboride (5 mils thick) attained ne highest surface temperature (4400 F), due to lower thermal conductivity and less heat capacity compared with most of the other coatings.

Coatings tested and results obtained are given in Table 39. Cu. of the eight coatings tested, two of them (LM-5 and W-2) did not protect the molybdenum from catastrophic oxidation under the test conditions*. The coating which exhibited the least damage was a flame-sprayed cermet coating of $90W-10ZrO_2$.

Bell Aircraft Corporation. [235, Vol III] The extensive investigations carried out at Bell, under the direction of Anthony and Pearl, to determine the feasibility of utilizing available heat-resistant materials for hypersonic leading-edge applications have been well reported elsewhere. [235] During the initial survey phase of this program, available information was reviewed on 106 materials which included 22 refractory metals and alloys and 30 protective coatings. Subsequently a screening-test program, which included three metals and five coating systems, was carried out to fill the gaps in available data and to provide consistent sets of data upon which to base selections. Using the data obtained experimentally and the methods developed for assessing suitability for the desired mission, refractory-metal coating systems selected for further evaluation from the then available materials were: W-2/Mo-0.5Ti and Durak MG/Mo-0.5Ti.

In follow-up work at Bell on these two systems, which is reported in detail in Reference 235, Vol VII, the pertinent conclusions reached were as follows:

(1) Not even the most promising of the then available coating systems possessed the high reliability required for use on critical components, such as leading edges, of manned, reusable hypersonic gliders.

(2) Of the two protective coatings evaluated on Mo-0.5Ti, W-2 and Durak MG, the former appeared to offer superior resistance.

(3) A major problem in the protection of the molybdenum alloy by the two coatings was the adequate protection of edges ard corners.

(4) Available inspection techniques were inadequate for determining the acceptability of the coated refractory materials investigated.

Southern Research Institute. [235, Vol IV] In line with the objectives of the work done at Bell, a mechanical-property study of bare and W-2 and Durak MG coated

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*The report of this work was ... d December, 196. More recently (May-June 1961)[258] it has been reported that W-2 successfully protected M -0.5Ti pro. in .. stream velocities above Mach 4 at temperatures of 3850 F for 45 seconds.

TABLE 39.   SUMMARY OF RESULTS FROM TESTING COATED MOLYBDENUM
FOR POSSIBLE USE AT 4000 F FOR 60 SECONDS[196]

Coating	Coating Thickness, mils	Method of Application	Observations[a]
Al-Si	10	Flame sprayed	Probe oxidized gradually during test. Except for slight erosion at front nose portion and a buildup of slaglike oxidation products, substrate was not visually damaged.
ZrB_2	5	Flame sprayed	Although probe attained the highest surface temperature (4400 F), no catastrophic oxidation occurred. Only apparent damage was cracking and very slight removal of coating along blunt nose radius. Slight erosion and deposition of a very thin film of oxidation products were visible.
W-2	1.4	Vapor diffusion	Coating started to flake off at blunt nose radius at early part of test, and catastrophic oxidation was observed just before test was completed.
Durak MG	1.4	Vapor diffusion	Superior to W-2 in that no catastrophic oxidation was observed during the test nor upon postexamination. Some slag or combustion residue present at the nose.
$MoSi_2$	1.4	Vapor diffusion	Fair over-all protection. Slight erosion and deposition of scale on blunt nose portion, and deposition of sublimation products at rear section.
$90W-10ZrO_2$	5	Flame sprayed	Exhibited least amount of damage of all coating systems tested. Coating ablated or sublimed slightly and uniformly at blunt nose. Postexamination showed coating blistered slightly.
LM-5	15	Flame sprayed	Coating flaked off at blunt nose radius during beginning of test, and was followed by catastrophic oxidation of substrate.
Gradated ZrO_2	15		Even though coating flaked off along blunt nose radius soon after test was started, no oxidation of substrate was observed during the test. Postexamination showed no apparent damage or oxidation of substrate. Coating adjacent to blunt nose was cracked. Evidently metal-rich inner layer of coating remained intact during test and was able to protect substrate from oxidizing.

(a) See text for outline of experimental procedure.

Mo-0.5Ti was carried out by Kattus, Preston, and Lessley. Their findings were as follows:

(1) Both coatings had an extreme embrittling effect and a weakening effect on the substrate at room temperature.

(2) At 1200 F and above, the coated material was equivalent in strength and only slightly less ductile than the bare metal.

(3) Under tension and compression loads, the coatings absorbed, without failure, elastic strain and varying degrees of plastic strain from less than 1 per cent up to 18 per cent depending on the conditions.

(4) Although the coatings could absorb considerable plastic strain under many conditions, further research was needed to safely extend their usefulness beyond small amounts of plastic strain at 2100 F and at room temperature.

Figures 37 through 41 were selected from the numerous graphs presented by Kattus, Preston, and Lessley on the mechanical properties of W-2 and Durak MG coated Mo-0.5Ti. They are self-explanatory with the exception of Figure 39. Due to variances in the experimental results, an averaging analysis of the stress-strain curves for bar material was done at the 0.002 in/in/min strain rate. The curves in Figure 39 represent the results of this averaging; and, as stated by the originators of this work, may be employed for coated or bare material in tension or compression.

The Marquardt Corporation. Preliminary tensile properties reported for uncoated and Durak MG, PFR-5, Pfaudler Cr, and W-2 coated Mo-0.5Ti are presented in Figures 42 and 43. No additional information on the identity of the Pfaudler Cr coating is available.
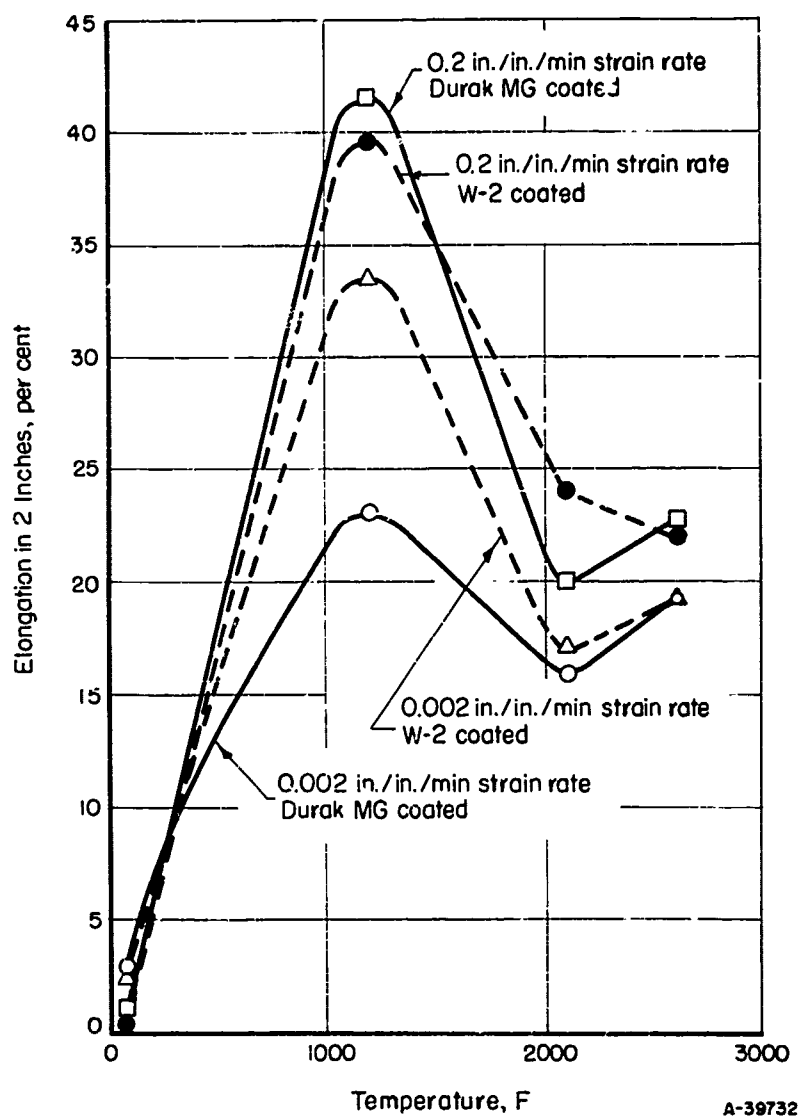
FIGURE 37. EFFECT OF TEMPERATURE ON TENSILE PER CENT ELONGATION OF W-2 COATED AND DURAK MG COATED MOLYBDENUM-0.5 PER CENT TITANIUM BAR, ARC CAST, FULLY RECRYSTALLIZED[235, Vol V]
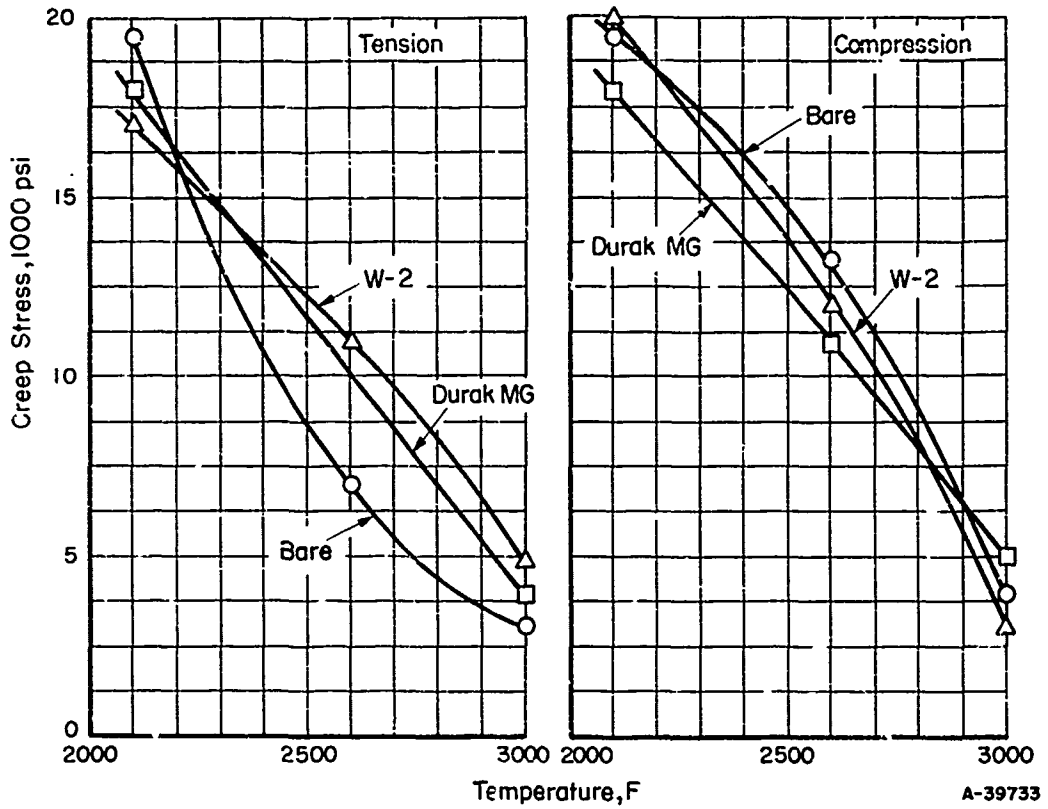
FIGURE 38. EFFECT OF TEMPERATURE ON THE STRESSES IN TENSION AND IN
COMPRESSION REQUIRED TO CAUSE 2 PER CENT CREEP STRAIN
IN 10 MINUTES IN BARE AND COATED MOLYBDENUM-0.5 PER
CENT-TITANIUM BAR, ARC CAST AND FULLY
RECRYSTALLIZED[235, Vol V]
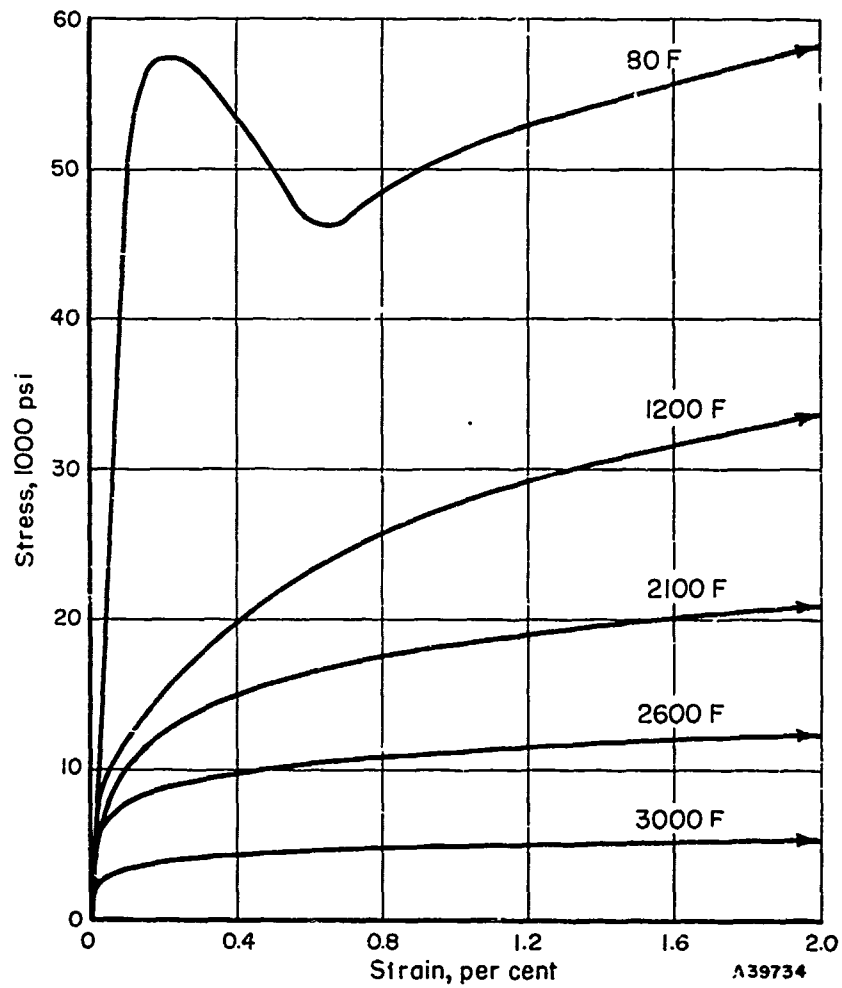
FIGURE 39. SUMMARY STRESS-STRAIN AT VARIOUS TEMPERATURES AND
0.002 IN. /IN. /MIN FOR UNCOATED. W-2 COATED, AND DURAK
MG COATED MOLYBDENUM-0.5 PER CENT TITANIUM BAR,
ARC CAST, FULLY RECRYSTALLIZED[235, Vol V]
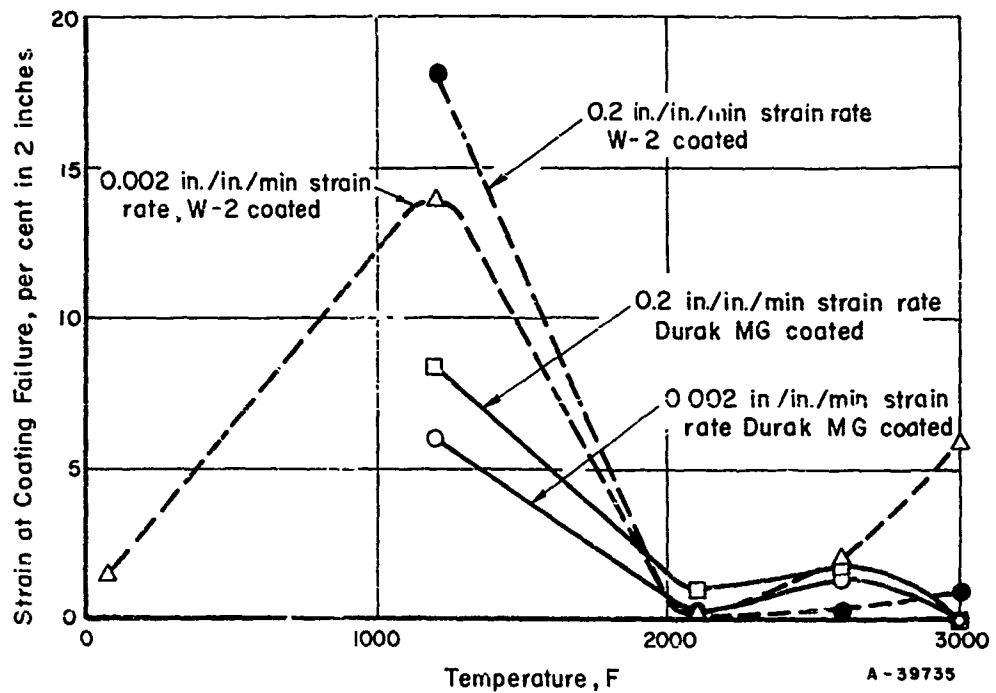
FIGURE 40. EFFECT OF TEMPERATURE ON THE STRAIN AT COATING FAILURE IN TENSION OF W-2 COATED AND DURAK MG COATED MOLYBDENUM-0.5 PER CENT TITANIUM (0.060-INCH SHEET), ARC CAST, FULLY RECRYSTALLIZED[235, Vol V]
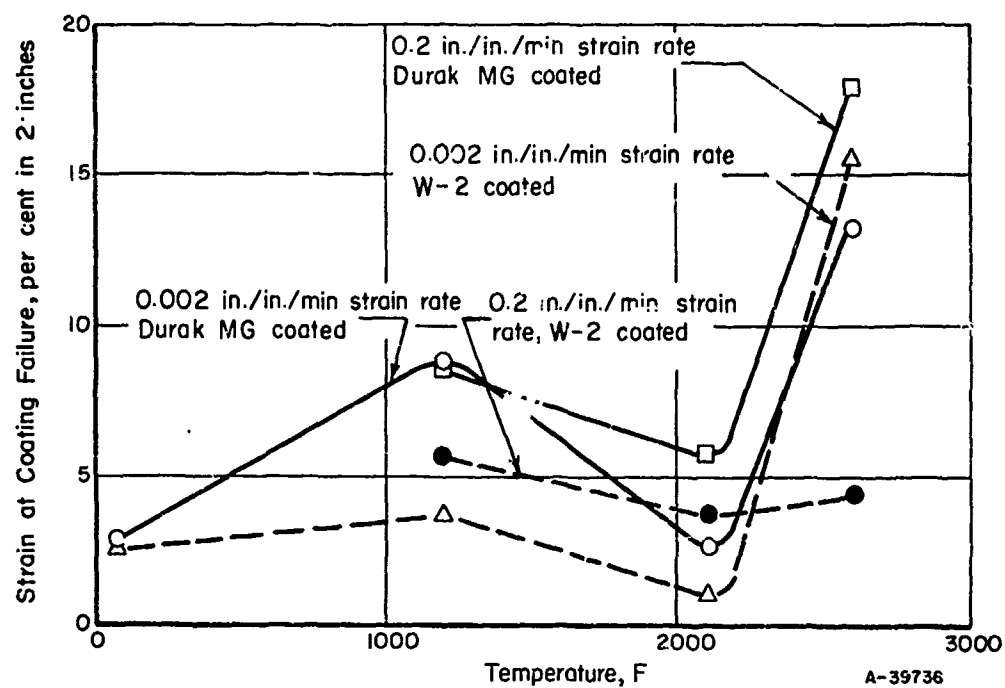
FIGURE 41. EFFECT OF TEMPERATURE ON THE STRAIN AT COATING FAILURE IN TENSION OF W-2 COATED AND DURAK MG COATED MOLYBDENUM-0.5 PER CENT TITANIUM BAR, ARC CAST, FULLY RECRYSTALLIZED[235, Vol 5]
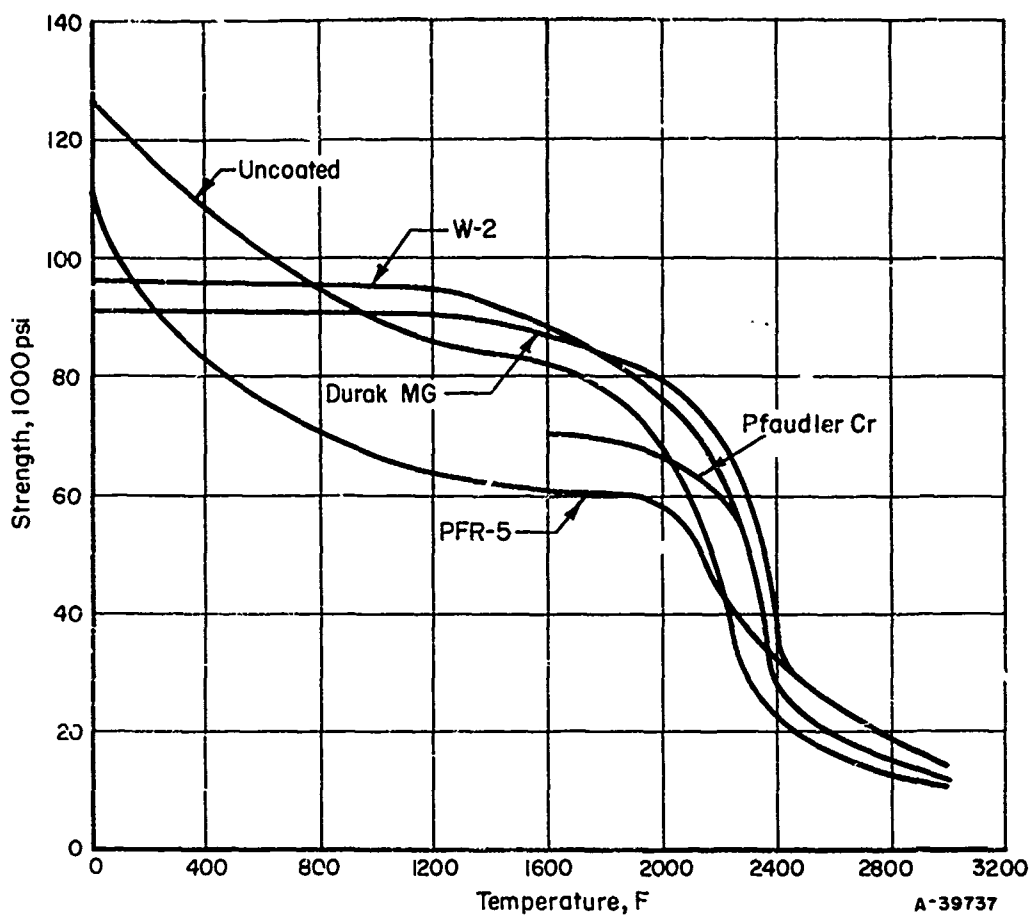
FIGURE 42. PRELIMINARY ULTIMATE TENSILE STRENGTH OF Mo-0.5Ti SHEET
UNCOATED AND WITH VARIOUS COATINGS[260]

Test Conditions:

      Machine - E.T.T.M.
      Method of Heating - Resistance
      Time to Test Temperature - 200 F/min
      Hold Time at Temperature - 5 min
      Strain Rate to YS - 0.001 in./in./sec
      Strain Rate From YS to UTS - 0.01 in./in./sec

Atmosphere

      Coated - Air
      Uncoated - Argon-7% hydrogen

Sheet Thickness - 0.050 - 0.060 in.

Gage Length - 2.0 in.
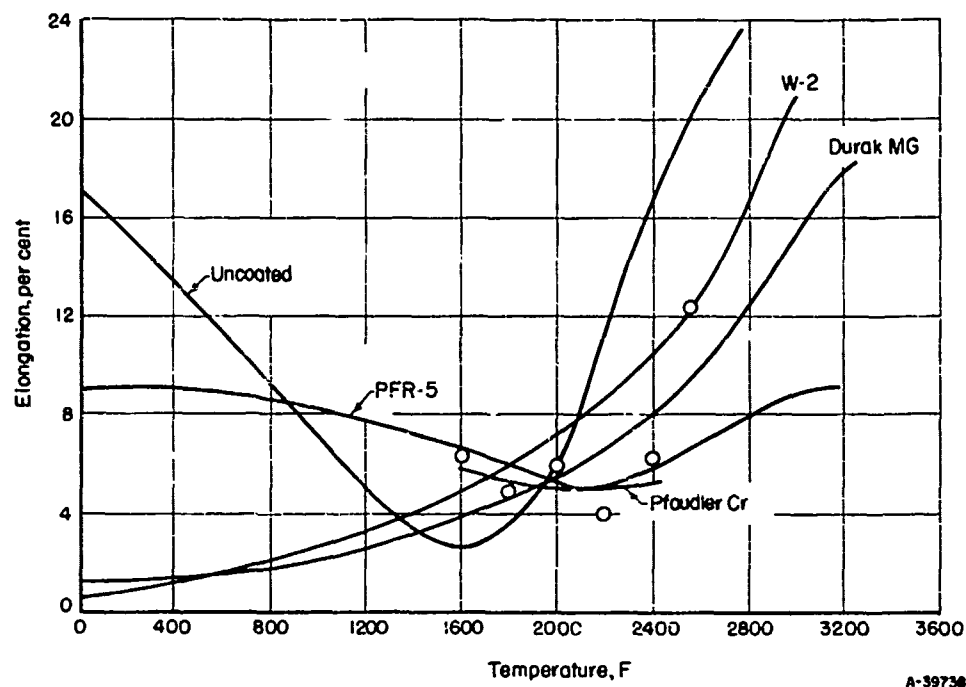
FIGURE 43. PRELIMINARY AVERAGE TENSILE ELONGATION OF Mo-0.5Ti SHEET
UNCOATED AND WITH VARIOUS COATINGS[260]

Test Conditions:
      Machine - E.T.T.M.
      Method of Heating - Resistance
      Time to Test Temperature - 200 F/min
      Hold Time at Temperature - 5 min
      Strain Rate to YS - 0.001 in./in./sec
      Strain Rate From YS to UTS - 0.01 in./in./sec

Atmosphere:
      Coated - Air
      Uncoated - Argon-7% hydrogen

Sheet Thickness - 0.050 - 0.060 in.
Gage Length - 2.0 in.

COATINGS FOR COLUMBIUM

Coatings for Columbium

Major research and development on protective coatings for columbium is recent relative to that for molybdenum. There is evidence to indicate that all coatings which appeared promising for molybdenum (and some which did not) were tried on columbium. Usually a good translation from one system to the other was not effected. There are three reasons for this:

(1) Major differences in coating-substrate chemistry (see remarks under Importance of Substrate Composition)

(2) Differences in thermal, physical, and mechanical properties

(3) Columbium (and tantalum) have appreciable solubility for oxygen and nitrogen which severely embrittles the substrate, and this "contamination" must be prevented as well as gross oxidation.

As with molybdenum, effort on protective coatings for columbium-base alloys has been directed toward aircraft gas-turbine and space-vehicle applications. Also, a very substantial amount of effort has been directed toward nuclear applications. One such application involves a low heat flux and enthalpy with long-time exposure. The environment is moving air at temperatures up to 2500 F, velocities to 15 feet per second, and pressures to 7 atmospheres. [273]

Due to security restrictions, much of the information generated for nuclear applications has not been made available for publication.

Metallic Coatings

Fe-, Ni-, and Co-base alloys have been investigated for the protection of columbium. In general, they suffer the same shortcomings as outlined for molybdenum systems (Tables 19 and 20).

Electroplated chromium is difficult to apply to some columbium-base alloys without excessive embrittlement. However it can be applied and used with a good deal of reliability for short-time application at 2500 F. [5]

TRW Cr-Ti-Si[201]. One of the recent major programs was carried out at the Tapco Division of Thompson Ramo Wooldridge by Jefferys and Gadd. This program, under sponsorship of the Air Force, had three major objectives:

(1) The further development of the TRW vacuum vapor process and coating

(2) The comparative evaluation of the most promising coatings available for columbium applied to the same substrate materials

(3) The general advancement of the state of the art of protective coatings for columbium and development of test procedures for evaluating the properties of a coating substrate system.

Information relative to the first objective is presented in this section of the report.

The TRW Cr-Ti-Si coating is applied by a pack process operated under vacuum at 2000 to 2450 F. The process can be operated to effect the transfer of the coating elements to the substrate, where they diffuse, via the normal vapor pressure of the elements or by a combination of normal vapor pressure plus volatile halide. Apparently, the latter, which gives the "KF activated" coating, is preferred because lower temperatures and shorter times can be employed More important, a continuous phase of CbCr$_2$ is formed and better alloying results in the coating, both of which appear to give much improved performance. An extensive evaluation of the variables in the process has been reported in detail elsewhere[201].

Figure 44 shows a schematic profile of the Cr-Ti-Si coating on columbium applied from an unactivated pack, and Figure 45 shows a schematic drawing of the coating applied from the activated pack.

Protective Life. Figure 46 shows the protective life of activated Cr-Ti-Si coatings on D-31 alloy at 2500 F as a function of silicon-alloy-layer thickness. The protective life of two activated coatings, Cr-Ti-Si and Ti-(Cr-Ti)-Si, on D-31, F-48, and columbium at 2300 and 2500 F is given in Table 40. Clearly, very substantial protection is indicated.

The superior performance of the activated and titanium-pretreated Cr-Ti-Si coatings on columbium substrates is due to two factors. The first is the formation of a continuous zone of CbCr$_2$ at the coating-diffusion zone interface that inhibits diffusion of oxygen inward and columbium outward. The second is the formation of a highly alloyed chromium-silicon region beneath the outer silicon layer which apparently heals the thermal and mechanical cracks produced in the coating on thermal cycling and supplies silicon to the outer SiO$_2$ layer on the surface.

Coating capabilities of the unactivated Cr-Ti-Si were investigated on D-31 alloy at temperatures of 2600 to 2800 F in air. Coated specimens were placed in platinum crucibles and exposed in a Globar heated furnace. The specimens were cycled to room temperature for observation at 1/2-hour intervals for the first 3 hours of test and at 1-hour intervals thereafter. All specimens at each temperature were initially exposed together, and individual specimens were withdrawn at the indicated time intervals. Table 41 lists the observations.

At 2600 F the coating surface gradually developed a glassy appearance with the first evidence of localized failure observed after 15 hours of exposure. The oxidation products of the coating formed a low-melting slag with Cb$_2$O$_5$ and melted in the region of the failure.

At 2700 F the glassy surface developed in less than 3 hours, with no evidence of failure in 5 hours. A spot had failed on the specimen removed at 3 hours; however, under low magnification in the microscope, it was observed that the region had apparently self-healed as a result of the glassy product on the coating surface flowing over and sealing the defect.

At 2800 F the coating surface was glassy after 1 hour with no evidence of coating failure. However, after 2 hours the coating had failed and melting of the oxidation products had occurred, partially destroying the specimen.
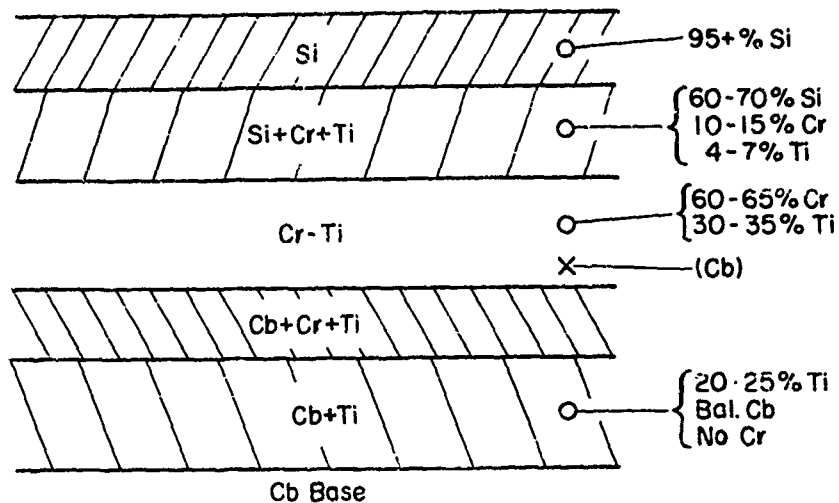
FIGURE 44. A SCHEMATIC PROFILE OF THE Cr-Ti-Si COATING AP. TO COLUMBIUM SHOWING ANALYSIS VALUES FOR THE VARIOUS REGIONS[201]
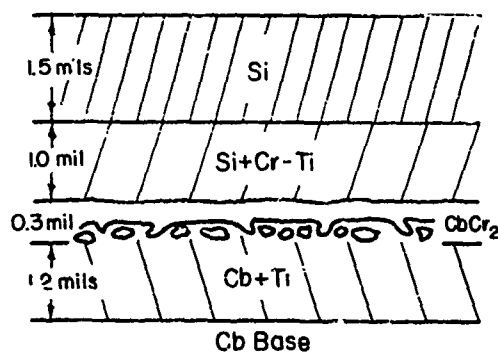
Activated Cr-Ti-Si Cooting

Cr-Ti(KF) 8 hours - 2300 F
Si(KF) 5 hours - 2100 F

FIGURE 45. SCHEMATIC DRAWING OF THE ACTIVATED Cr-Ti-Si COATING AS IT FORMS[201]
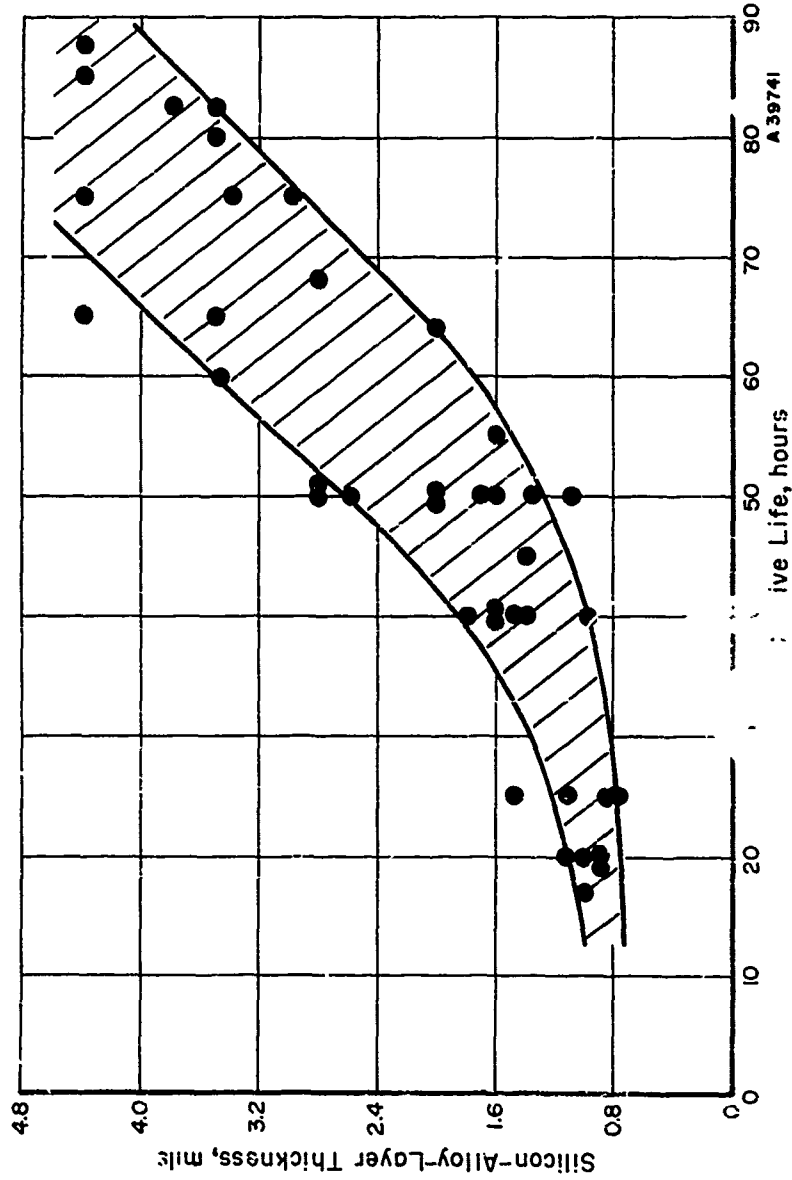
FIGURE 46. PROTECTIVE LIFE OF A... :) Cr-Ti-Si COATINGS ON D-31 ALLOY AT 2500 F AS A FUNCTION OF SILICON-ALLOY-LAYER THICKNESS(201)

(Specimens cycled to room temperature eight times in every 24-hour period and inspected thoroughly.)

TABLE 40. PROTECTIVE LIFE OF ACTIVATED Cr-Ti-Si AND
Ti-(Cr-Ti)-Si COATINGS ON D-31, F-48 AND
UNALLOYED COLUMBIUM AT 2300 AND 2500 F[201]

| Alloy | Oxidation Temperature | Protective Life[a], hours | |
		Cr-Ti-Si[b]	Ti-(Cr-Ti)-Si[c]
Cb	2500	70-80	>90
F-48	2500	70-80	>90
D-31	2500	80-90	>90
Cb	2300	90-110	140-160
F-48	2300	90-110	240
D-31	2300	140-180	240

(a) Indicates point of initial failure. Minimum of two specimens per condition. At 2500 F tests were terminated at 90 hours with no failures on any of the titanium-prea ed cimens. Specimens were cycled to room temperature eight times in every 24-hour period and in   thoroughly.

(b) Cr-Ti (KF activated), 8 hours at 2300 F
    Si (KF activated), 12 hours at 2150 F.

(c)   Ti (KF activated), 3 hours at 2200 F.
    Cr-Ti (KF activated), 8 hours at 2300 F.
    Si (KF activated), 12 hours at 2150 F.

TABLE 41. OXIDATION OF Cr-Ti-Si[a] COATED D-31 IN AIR AT 2600 F AND ABOVE[201]

Temperature, F	Exposure[b] Time, hours	Remarks
2600	1	No evidence of failure, rough surface
	3	No evidence of failure, rough surface
	11	No evidence of failure, glassy surface
	15	Spot failure, oxide product melted, glassy surface
2700	1	No evidence of failure, rough surface
	3	Spot failure, evidence of self healing, glassy surface
	5	No evidence of failure, glassy surface
2800	0.5	No evidence of failure, rough surface
	1.0	No evidence of failure, localized areas glassy
	2.0	Partial destruction of the specimen by melting of the oxide products

(a) Cr-Ti coated, 24 hours at 2350 F
   Si coated, 16 hours at 2200 F.
(b) Cycled to room temperature at 1/2-hour intervals for the first 3 hours, and then every hour thereafter. Tests terminated at indicated times.

Thermal-Shock Studies. Curved 60-mil D-31 alloy-sheet specimens were coated with Cr-Ti-Si, Cr-Ti-Al-Si, Cr-Ti-Si+Al$_2$O$_3$ (plasma sprayed), and Cr-Ti-Al-Si+Al$_2$O$_3$ (plasma sprayed). The coating sheet specimens were thermal-shock and erosion tested by heating to 2500 F in about 18 to 20 seconds in an oxidizing oxyacetylene flame and cooling rapidly in a high-velocity air blast in about 10 to 12 seconds to approximately 250 F. Cooling to lower temperatures involved more time and was not considered effective in producing further thermal shock. The heating and cooling rates were quite high, and severe thermal stresses were imposed on the thin curved sheet sections and between the coating and the base metal. On heating, because of the contour, the outside (front) of the specimen was in compression and the inside (back) was in tension. On cooling, the direction of the stresses reversed.

Specimens were tested for 100, 500, and 1000 cycles from 2500 to 250 F. Several specimens were given an additional exposure at 2500 F for 1 hour to intensify any coating failure. No coating failures were observed for either the Cr-Ti-Si or the Cr-Ti-Al-Si coating in 100 or 500 cycles. Metallographic examination indicated no oxygen contamination beneath the coatings prior to or after the 1-hour exposure at 2500 F. However, a large number of cracks appeared in the coating on the back side (compression on cooling) of specimens tested 500 cycles. These cracks at this stage did not penetrate into the diffusion zone. The plasma-sprayed Al$_2$O$_3$ outer coatings did not survive 100 cycles from 2500 F. The layer cracked and spalled. Because of this poor behavior and the difficulties of plasma or flame spraying other than cylindrical forms, further work was not attempted in this area and emphasis was concentrated on the more promising vacuum vapor-deposited coating.

After 1000 cycles, localized coating failure was evident on the front side of the Cr-Ti-Si and Cr-Ti-Al-Si coated specimens in the flame impingement area. Failure was apparently due to the growth of cracks in the coating layer. On prolonged cycling these cracks propagate into the base metal, permitting oxidation to proceed beneath the coating. As oxidation continues, the transition temperature of the oxygen-affected zone increases, rendering the metal adjacent to the cracks more susceptible to thermal shock, and the cracks continue to propagate.

Hot-Gas Erosion Studies. In order to determine the stability and oxidation resistance of the Cr-Ti-Si coatings under high velocity and high heat-flux conditions, coated curved sheet specimens were exposed to the exit stream of a 60 kv Thermal Dynamic plasma flame generator. One set of reproducible conditions was chosen for a standard test. These were as follows:

Generator and Gun Assembly:

Electrodes — tungsten
Nozzle opening — 13/64-in. diameter
Gas flow — 100 ft^3/hr N$_2$
            25 ft^3/hr O$_2$
Amperes — 300
Volts — 66.

Gas Stream:

    Composition — 80% N_2 and 20% O_2 (simulated air)

    Velocity — 1800 to 2200 ft/sec

    Heat flux — 300 to 340 Btu/(ft²) (sec) (1/2-inch diameter cold
      copper calorimeter).

Specimen:

    Distance from nozzle — 1 inch

    Front-side surface temperature — 2500 to 2550 F

    Back-side surface temperature — 2400 to 2430 F (argon cooled)
      (temperatures were measured with an optical pyrometer)

    Heat flux through specimen — 150 to 180 Btu/(ft²)(sec)
      (based on an assumed thermal conductivity value for the
      coating of 350 Btu/(hr)(ft²)(F)/(in.).

Under these operating conditions, a deposit that reduced effective cooling was built up in the throat of the nozzle after 30 minutes of continuous operation. Severe pitting occurred and in one case a nozzle melted. During the long-duration exposures, the test was stopped every 20 minutes to clean the nozzle. The specimen also received periodic thermal shock every 20 minutes in cooling to room temperature. With this procedure nozzles lasted for several 2-hour test runs totaling 6 to 8 hours of operation.

A series of Cr-Ti-Si coated D-31 alloy test specimens was prepared. Specimens were tested for 20 minutes, 1 hour (three 20-minute exposures), and 2 hours (six 20-minute exposures) under the above conditions. No coating failures occurred on any of the specimens up to 2 hours. To further evaluate the effect of the hot-gas erosion test on the Cr-Ti-Si coating, specimens were further exposed up to 33 hours at 2500 F in the cyclic-oxidation-furnace tests. No observable coating failures occurred on these specimens after exposure at 2500 F following the plasma test; however, microstructural examination of the specimens did reveal some oxygen penetration in the grain boundaries of the base metal that was not present previously.

An uncoated D-31 alloy specimen exposed under the above conditions autoignited and burned in 7 seconds. Unprotected tungsten and molybdenum sheet lasted about 12 to 15 seconds.

In order to test the Cr-Ti-Si coating at higher surface temperatures, the operating conditions of the plasma generator were held the same and the specimen was moved closer to the nozzle. One specimen was tested for 1 hour and another for 2 hours at 2600 and 2650 F. No coating failure occurred.

One Cr-Ti-Si coated specimen was moved closer to the nozzle in 50 F increments, allowing 3 minutes at each position for the temperature to stabilize. The specimen was held above 3000 F for approximately 10 minutes at an estimated surface gas velocity of 2500 ft/sec. Melting of the surface occurred above 3100 F and the specimen ignited and burned.

Intermetallic Coatings

Information on silicide-, aluminide-, and zinc-base coatings is presented in this section. The silicide- and aluminide-base coatings have indicated much potential for

protecting columbium-base alloys in the higher temperature ranges. Zinc-base coatings, although they have some very unique properties, have a top temperature limit of about 2050 F.

Silicide-Base Coatings. Techniques used for applying silicide-base coatings to columbium alloys have been vapor deposition (pack, fluidized bed, and vapor plating) and flame spraying. As with molybdenum, the pack-cementation technique has been used extensively and is very popular. For convenience of presentation, the coatings applied by vapor-deposition techniques will be discussed first, in alphabetical order by coating vendor, followed by the flame-sprayed coating.

The Thompson Ramo Wooldridge Cr-Ti-Si coating previously discussed could also be classified as a silicide-base coating.

Boeing Airplane Company.[226b, 244b] Silicide coatings are applied by the Disil-3 and fluidized-bed processes. The Disil-3 process, in which the reacting iodine is introduced into an evacuated retort containing silicon and the substrate at 1900 F, was designed primarily for columbium to overcome contamination problems. As reported[226b], the ductility and substrate contamination should not be appreciably altered by the process; however, the coated metal has less elongation than the bare metal.

In the fluidized-bed process, volatilized iodine flows through a heated silicon bed containing the substrate to be coated.

Oxidation lives of up to 3 hours at 2700 F have been reported for siliconized FS-82.

Chance Vought Corporation.[223] Under Air Force sponsorship, Chance Vought currently is carrying out a statistically designed development program to optimize its coatings for columbium and to improve reliability and reproducibility. The pack-cementation method is used.

Oxidation testing is being done primarily in a muffle furrace because it was found that "the environment of the exposure can have a profound effect on the apparent durability of the coating. Previous experience has indicated that the common means of heating the specimen in an oxyacetylene flame is unsatisfactory because of the difficulty in determining the oxidizing characteristics of the flame".

Preliminary information from this program is given in Tables 42 and 43. Tentative conclusions reached thus far in the program are as follows:

(1) Oxidation-resistance tests indicate that a silicon first coat followed by either a boron-chromium coating or a chromium-aluminum coat offers the best promise for an oxidation-resistant coating at 2600 F.

(2) Limited bend tests indicate these coatings affect the minimum radius to which the 0.020 inch-thick Cb-1Zr columbium alloy sheet can be bent without breaking. Uncoated sheet was bent to less than 1/2-inch radius at -100 F without breaking. Specimens coated with Si-B-Cr failed when bent to a 1.1-inch radius at -100 F. The specimens

TABLE 42. PRELIMINARY OXIDATION-RESISTANCE TESTS ON COATED Cb-1Zr SPECIMENS[223]

Deposited Component of Coated Material		Oxidation Exposure		Average Specimen Weight Increase, $mg/cm^2/hr$	Remarks
First Cycle	Second Cycle	Time	Temp, F		
60% Si	40% Cr, 20% B	5-1/2	2300	0.32	Slight edge failure
30% Cr, 30% Al	60% Si	1/2	2600	--	Coating melted
6 % Si	50% Cr	1/2	2600	2.4	Destroyed by melted coating from adjacent specimens
50% Si, 10% Al	None	1/2	2600	--	Coating melted
60% Si	None	1/2	2300	--	Coating melted
55% Si, 5% Y	30% Cr, 30% Al	4	2300	1.1	Small blister formed — oxidation underneath
20% B	60% Si	1/2	2300	--	Coating melted
60% Si (O)[a]	30% B, 30% Cr	5-1/2	2300	1.8	Slight oxidation along edge of specimens
		3	2600		
60% Si (P)[a]	35% Cr, 20% Al	5	2600	1.0	Slight oxidation along edge of specimens
6% Si	25% Cr, 25% Al	2	2600	1.48	Tests continuing

Notes:
Balance of pack consisted of Al_2O_3 and halides.
All coatings were made in furnace at 1900 ± 25 F for 16 hours.

(a) Coating formulations selected for further evaluation.

TABLE 43. PRELIMINARY INFORMATION ON ROOM-TEMPERATURE
STRENGTH OF 0.020-INCH-THICK COATED AND
UNCOATED Cb-1Zr COLUMBIUM[223]

Specification No.	Coating	0.2% Offset Yield Strength, psi	Ultimate Strength, psi	Elongation in 1 Inch, %
1	None	28,200	48,900	16
2	None	28,200	46,900	18
		Avg 28,200	Avg 47,900	Avg 17
0-1	Formulation O	29,400	49,800	19
0-2	Formulation O	28,100	50,300	22
		Avg 28,750	Avg 50,050	Avg 20
P-1	Formulation P	28,600	49,000	20
P-2	Formulation P	31,000	49,400	--(a)
		Avg 29,800	Avg 49,200	Avg 20

Note:
Specimens were taken transverse to the rolling direction.

(a) Specimen broke outside middle one-third.

coated with Si-Cr-Al failed when bent to a 1-inch radius at -100 F. However, it is believed this minimum radius is adequate for necessary flexing operations on the coated sheet material.

(3) Load-cycle tests indicate the coatings have enough ductility at elevated temperatures to afford protection to columbium specimens stressed just below the yield strength of the metal. This coating ductility allows the coating to follow the expansion and contraction of the metal without cracking and exposing the metal to oxidation.

(4) Metallographic examination shows there is no significant recrystallization of the Cb-1Zr at coating-process temperatures now being used.

Coating Formulations O and P (Table 42) have been selected for further evaluation. A wide variation in coating life was noted between specimens coated in different runs using nearly the same pack composition and even between specimens coated in the same run. It is believed that this can be remedied in large measure during succeeding months of the program.

Chromalloy Corporation. [226c] Modified W-2 coatings, applied to columbium-base alloys by pack cementation have survived over 200 hours at 2000 F, and over 125 hours at 2500 F. The greatest shortcoming of the coated columbium currently produced by Chromalloy has been the brittleness induced in the substrate by the coating process. This effect is thought to be caused by the susceptibility of columbium-base alloys to embrittlement by air. During the heat up portion of the coating cycle, the work pieces are contacted by the residual air present in the retort.

In some columbium materials it has been possible to restore ductility by a post-coating heat treatment. Some alloys (particularly D-31) are severely embrittled by air, and it has not been possible as yet to restore ductility by heat treatment.

Chromizing Corporation. [201] Durak Cb, a modification of Durak MG, is applied from a retort pack using hydrogen as a carrier gas. The melting point and emittance of Durak Cb is reported to be higher than that of modified W-2.

Few data are available for Durak Cb on columbium alloys. Specimens of a Cb-6Ti-0.75Zr alloy were coated with Durak Cb and oxidation tested by Boeing Aircraft Company. The coated specimens showed some oxidation in 1 hour at 2500 F and complete failure at 2700 F. Durak Cb coated FS-82 alloy sheet samples were evaluated by the Martin Aircraft Company. The coated FS-82 sheet was exposed for 15- and 30-minute cycles at 2950 F in air. In 15 minutes, no coating failure was evident and complete room-temperature ductility was retained. After 30 minutes the coating had failed over 50 per cent of the specimen edge.

Fansteel Metallurgical Corporation. [201, 254] Two silicide-base coatings for columbium alloys have been investigated at Fansteel: (1) S-2, or "conversion" coating, and (2) M-2, or "duplex" coating. The latter has given the better performance.

The S-2 or "conversion" coating is formed by siliciding the substrate surface at about 2550 F from a gas phase containing silicon tetrachloride and hydrogen, using induction heating. Protection of columbium alloys at 2300 F for 20 hours has been reported for S-2.

The M-2 or "duplex" coating is formed by: (1) deposition of MoO_3 by immersing the substrate in liquid MoO_3 at 1470 F, (2) reduction of the MoO_3 to molybdenum in hydrogen at 1470 F, and (3) siliciding from a gas phase as for the S-2 coating. The resulting coating consists of an outer layer of $MoSi_2$ and inner layers of substrate silicides. Protection from oxidation at 2300 F for about 40 hours has been reported.

Two modes of coating failure have been observed: (1) premature breakdown in isolated areas due to imperfections, and (2) uniform breakdown characterized by uniform scaling. In all cases, uniform breakdown occurred with the disappearance of the disilicide layer.

The lifetime to uniform failure of conversion-coated FS-82 is shown in Figure 47, for a 1.5 to 2-mil coating.
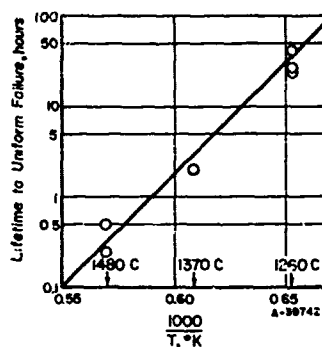
FIGURE 47. LIFETIME TO UNIFORM FAILURE OF FANSTEEL CONVERSION COATED FS-82 ALLOY[254]

Similar "lifetimes" for different substrates at 2300 F were reported as follows:

Substrate	Coating	Lifetime to Uniform Failure at 2300 F, hr
Cb	Conversion	7
	Duplex (MoO_3 vapor treated)	25
Cb-32Ta-0.7Zr (FS-82)	Duplex (MoO_3 liquid treated)	70
Cb-20Ta-4.5W-0.6Zr	Conversion	40
	Conversion	37
	Duplex (MoO_3 liquid treated)	70

Pfaudler Company. [226c] Single-cycle and double-cycle pack-cementation proc-esses have been used at Pfaudler for coating columbium-base alloys.

Coatings are applied to D-31, Cb-1Zr, FS-82, F-48, C-103, and columbium by two-cycle processes. The first cycle consists of a precoating cementation treatment, and the second cycle is a codeposition of silicon and an alloying element.

A single-cycle codeposition coating also is used for FS-82.

Table 44 summarizes the results to date obtained from these coating systems.

The following problems and difficulties were reported to have been encountered but overcome in providing protective coatings for columbium alloys:

(1) Occlusion of hydrogen by the substrate.

(2) Nitrogen contamination of the substrate due to use of ammonium salts as activators in the pack-cementation technique.

(3) Formation of undesirable products and hindered diffusion due to the large amounts of alloying elements used to produce structural alloys. For example, the diffusion rates of certain elements.are reduced by the presence of titanium and zirconium in the substrate.

Union Carbide Metals Company and Linde Company. [44, 201] A coating of LM-5 (40Mo-40Si-8Cr-2B-2Al), which was primarily developed by Linde for molybdenum, protected columbium in static exposure for about 1000 hours at 2100 F and for 100 hours at 2730 F. The coating, which was 4 to 8 mils thick, was applied by the Plasmarc process or by detonation gun.

Self-healing properties and thermal-shock resistance were improved by putting a 4 to 5 mil layer of D-945 (44Cb-32Ti-15Cr-5V-4Al) between the LM-5 and the substrate. This duplex coating system retained the static oxidation resistance of LM-5.

It was believed that the thermal-shock resistance and self-healing properties were due to a small amount (5 to 10 volume per cent at 2200 F) of liquid phase in the intermediate layer, and that this amount was sufficient to absorb and to even out the shear stresses produced during thermal cycling. Some experimental evidence indicated that the amount of liquid phase decreased as a result of oxygen contamination. Detailed experimental results for these coating systems are reported elsewhere[44].

Inasmuch as the coating is applied by spray processes, its application is limited to simple configurations. Quality coatings cannot at present be applied to most commercially significant components.

Aluminide-Base Coatings. The following techniques have been used to good advantage to apply aluminide-base coatings to columbium alloys:

(1) Hot dipping followed by diffusion anneal

TABLE 44. COATINGS FOR COLUMBIUM AND COLUMBIUM-BASE ALLOYS(226c)

Substrate	Coating Designation	Oxyacetylene Torch Oxidation Test Life		
		At 2600 F(a)	At 2800 F(a)	At 3000 F(a)
D-31 (2 cycles)	PFR-1A-D-31	Few min-3 hr		
	PFR-2A-D-31	Few min-13 hr		
	PFR-3A-D-31	5-28 hr		
	PFR-4A-D-31	2-14 hr		
	PFR-1-D-31	5-14 hr		
	PFR-2-D-31	15.8 hr and 15.3 hr (Two samples tested)		
	PFR-1M-D-31	16.3 hr and 26.3 hr (Two samples tested)	5-11 hr	2-4 hr
FS-82 (1 cycle)	PFR-1S-FS-82	2-6 hr		
FS-82 (2 cycles)	PFR-1M-FS-82	The same as above or slightly better		0.5-0.75 hr
Cb-1%Zr (2 cycles)	PFR-1M-Cb-1Zr	3-4 hr	1-4 hr	0.5-4 hr
C-103 (2 cycles)	PFR-2M-C-103	Coated 5 mil-thick foil did not fail after 3 hr	0.5-1 hr	
Cb (2 cycles)	PFR-2M-Cb	3.5-6 hr		0.5-1 hr
F-48 (2 cycles)	PFR-2M-F-48			0.25-1 hr

(a) Temperatures were measured with optical pyrometer assuming coating emittance of 1.0.

(2) Paint (slurry dip, cold spray, brush) and diffusion anneal

(3) Pack cementation.

The paint and diffusion-anneal technique has had a recent upsurge of activity. The hot-dipping technique has been in existence for some time, and probably has been at least superficially looked at by most people working in the protective-coatings field.

Boeing Airplane Company.[226b] The hot-dip process at Boeing consists of dipping the substrate in a molten Al-Si bath and subsequently diffusing the coating at 2200 F in a protective atmosphere. Substrate properties have been reported to be essentially unaffected by the coating process. Oxidation protection has been obtained for over 1 hour at 2600 F in static air.

Chromalloy Corporation. Pack cementation has been used to apply aluminide-base coatings to columbium alloys. Some of these coatings have withstood 2500 F for over 25 hours, but they have not appeared to be impervious to the diffusion of oxygen. In some instances, weight gains of 100 or more mg have been recorded on apparently sound specimens (1 inch x 0.5 inch).

General Electric Company, FPLD. Two aluminide-base coatings for columbium alloys have been reported by GE: Aldico coatings and the LB-2 coating.

Carlson[203] reported on the processing and performance of aluminum dip-coated (Aldico) columbium alloys. Time (1 to 13 min) and temperature (1500 to 2100 F) for dipping in an Al-15Si bath, in a graphite crucible and covered with Alcoa No. 30 brazing flux, and posttreatment procedures were evaluated. The results indicated the optimum dip time, temperature, and posttreatment to be respectively, 3 min at 1695 F and a treatment in vacuum for 1 hour at about 1900 F. Alloys studied were F-48, F-50, FS-82, Cb-7.5Ti-5Mo and Cb-8Ti. Information on processing parameters and oxidation resistance is presented in Figures 48 through 53. X-ray diffraction analysis of the coating on Cb-7.5Ti-5Mo after posttreatment indicated the presence of $CbAl_3$ and $(Cb, Ti)Al_3$ along with free silicon and aluminum; $CbAl_3$ and $TiAl_3$ are isomorphous. Aldico coatings on substrates containing titanium were more oxidation resistant than those on alloys not containing titanium.

The LB-2 coating was developed at GE, in conjunction with the McDonnell Aircraft Company, to protect a complex replica of a fixed fin-deflecting rudder assembly made of F-48 alloy. Target requirement for the coating was protection for 4 cycles with a total time of 2 hours at 2500 F. Although the final proof of the merits of the coating system, namely satisfactory performance in flight, has not been determined, there are good reasons for confidence that such performance will be forthcoming.

A test of the assembly was made at McDonnell on July 15, 1961.[226c] All test objectives were not met because the heating equipment was overtaxed. The assembly withstood several cycles of temperatures up to 2425 F and several load cycles up to 150 per cent of design ultimate load. There was localized skin wrinkling in 5 or 6 panels of the assembly, and approximately 10 panel corners were warped. The coating held up well, and no type of structural failure appeared to be imminent.
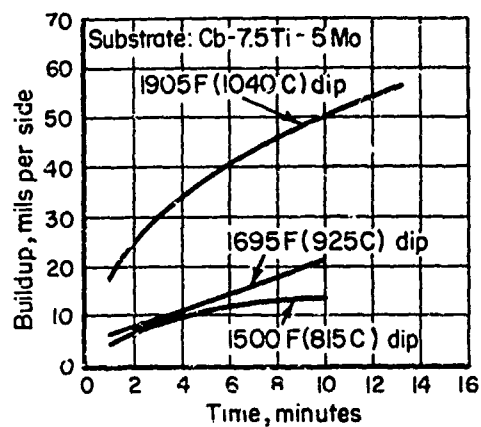
FIGURE 48. EFFECT OF TIME OF DIP ON BUILDUP[203]

Posttreatment: 1 hr, 1900 F, specimens nestled in $89Al_2O_3-10Al-1NH_4Cl$ in an uncovered Inco 702 boat in argon.
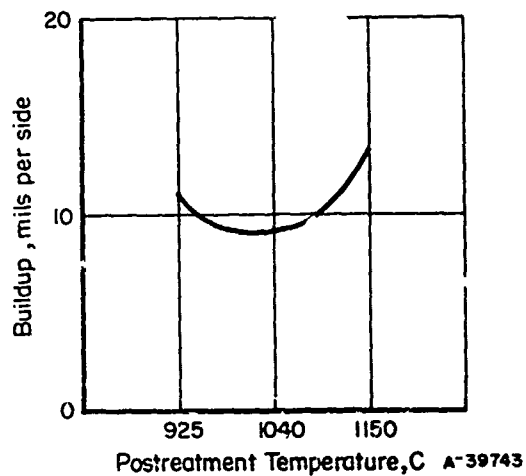
FIGURE 49. EFFECT OF POSTTREATMENT TEMPERATURE ON BUILDUP (925 C DIP, 3 MIN)[203]

Substrate and posttreatment procedure the same as in Figure 48.
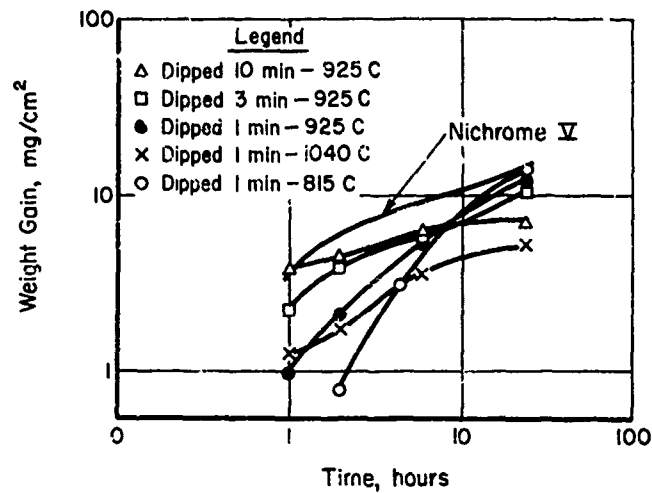
FIGURE 50. OXIDATION OF ALDICO-TREATED 7.5Ti + 5Mo-Cb ALLOY, 1260 C (2300 F) STATIC AIR[203]

Posttreated at 1040 C for 1 hour with procedure given for Figure 48.
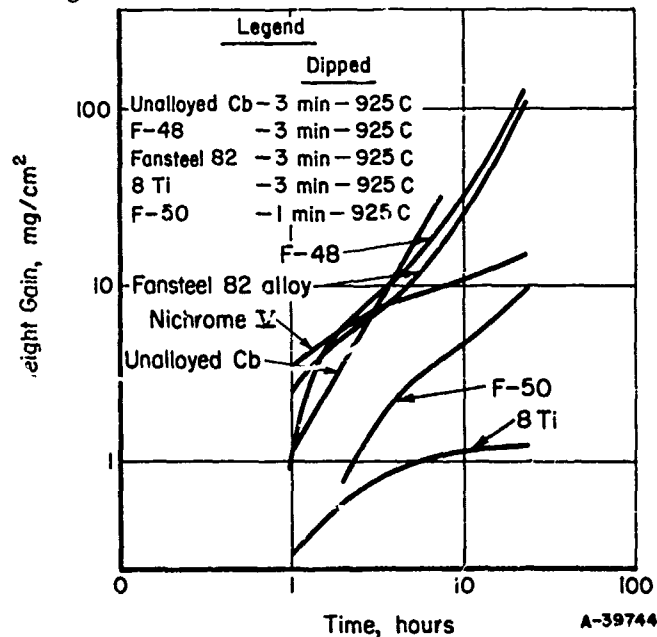
FIGURE 51. OXIDATION OF ALDICO-TREATED Cb AND Cb ALLOY, 1260 C (2300 F) STATIC AIR[203]

*Posttreated at 1040 C for 1 hour with procedure given for Figure 48 except Inco 702 boat was covered
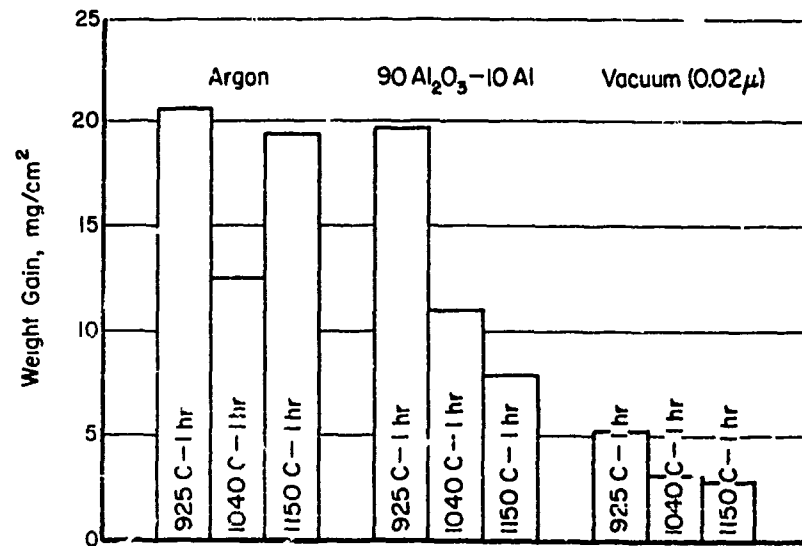
FIGURE 52. WEIGHT GAINED AFTER 2-HOUR OXIDATION, 1370 C (2500 F) STATIC AIR, FOR ALDICO COATED (3 MIN, 1800 F) FS-82 GIVEN VARIOUS POSTTREATMENTS[203]
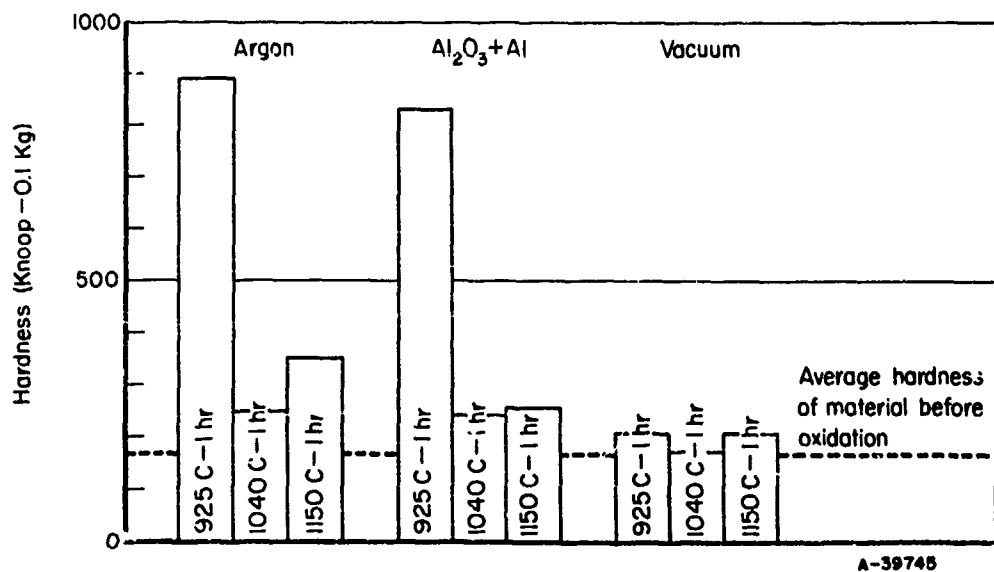
FIGURE 53. HARDNESS OF ALDICO COATED (3 MIN, 1800 F) FS-82 GIVEN VARIOUS POSTTREATMENTS AFTER 2-HOUR OXIDATION, 1370 C (2500 F) STATIC AIR[203]

An outline of the process used for applying the LB-2 coating was given under "Preparation of Coating Systems, Paint and Sinter or Diffuse". Preparation procedures for the substrate prior to coating application were discussed in "Refractory Metal Substrates for Coating Systems, Importance of Substrate Preparation". The process is essentially a paint (cold dip in slurry, cold spray, or brush) and diffuse technique. Other process intricacies and details have been reported elsewhere[211-213].

The as-prepared coating on F-48, after diffusion annealing, has a two-layer structure. The composition of the individual layers has not been determined, but from previous work at GE, it would appear that the layer adjacent to the substrate is predominantly complex intermetallics of $(Cb, Cr)_2Al$, $(Cb, Cr)Al$, and $(Cb, Cr)Al_2$. The outer layer would be primarily $(Cb, Cr)Al_2$ and $(Cb, Cr)Al_3$. The silicon present in the prediffused coating serves primarily to improve the fluidity of the coating alloy in providing complete and uniform flow over all surfaces during the annealing treatment.

The LB-2 coating has been reported by GE[213, 226b] to protect FS-80, FS-82, F-48, F-50, and Cb-65 columbium-base alloys from oxidation and contamination for a minimum of 2 hours at 2500 F in static air. An F-48 panel was double coated and exposed for 15 minutes at 2900 F; the appearance of the panel after the test was excellent, with no evidence of any oxidation. Boeing has been reported[244b] to have found a 1 to 2-hour protective life at 2700 F for FS-82 coated by the GE LB-2 coating. North American Aviation, Los Angeles, reported the following results for single test coupons of FS-82 coated with LB-2. [267]

Test	Temperature, F	Results
Thermal cycle[a]	2600	4 cycles with 0.6 per cent weight gain. General failure.
Erosion[b]	2600	45 minutes with 5.6 per cent weight loss. Edge failure only.

(a) A succession of 1.5-hour thermal cycles (each cycle including 0.5 hour at temperature) in a static, sea-level, air environment.
(b) Continuous exposure to a high-velocity gas stream.

Tensile properties of LB-2 coated F-48 and FS-82B sheet are given in Figures 54 and 55, respectively.

North American Aviation, Inc., Los Angeles. A paint and diffuse aluminide-base coating also has been under development at North American for columbium-base alloys.[226b, 267] A coating slurry, composed of a mixture of aluminum and ceramic powders in an organic vehicle, is applied by spraying, dipping, or brushing. After drying, the slurry-coated parts are heated to 1900 F in argon for 1 hour.

In preliminary oxidation testing, aluminized FS-82 alloy specimens were exposed at 2600 F for 3 hours in a static oxidizing atmosphere without visible harmful effects.

Tensile coupons of aluminized FS-82 were subjected to various elevated-temperature exposures and then tested at room temperature. The tensile properties thus determined are listed below, in comparison with unheated materials:
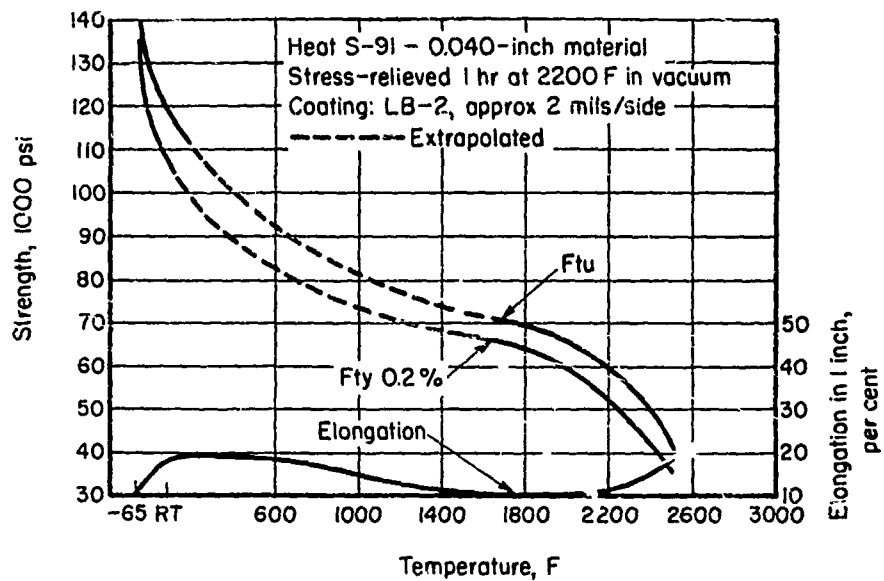
FIGURE 54. TENSILE PROPERTIES OF LB-2 COATED F-48 ALLOY SHEET[275]
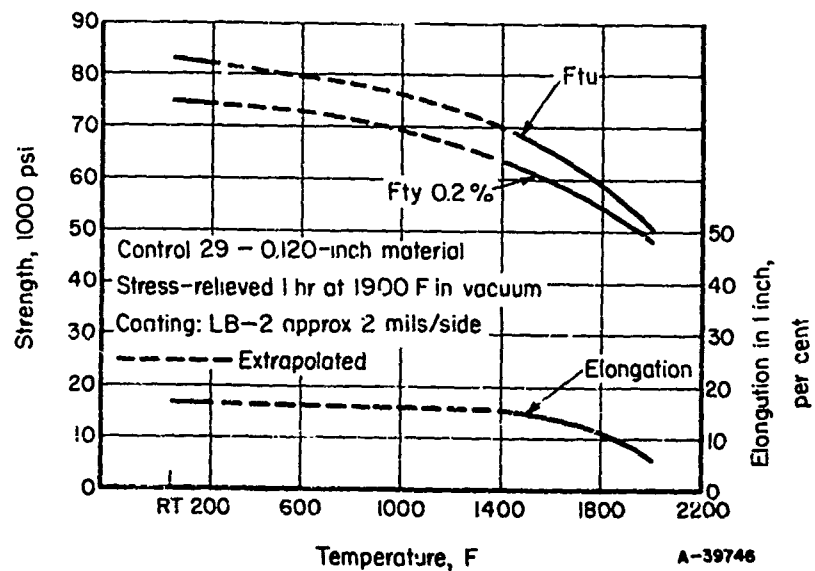
FIGURE 55. TENSILE PROPERTIES OF LB-2 COATED FS-82B ALLOY SHEET[275]

Exposure		Strength, 1000 psi		Elongation in
Temp, F	Time, hr	Ultimate	0.2% Yield	2 In., %
1850	1	64.9	45.0	23.5
1850 plus 2540	1-1/2	69.0	54.8	22.9
1850 plus 2580	5	74.5	62.1	25.4
(Unexposed, uncoated base metal)[a]		68.4	47.6	19.8
(Unexposed, coated)[a]		64.0	43.7	18.5

(a) Control tests.

The above results are preliminary in nature and represent single-point data. However, the data indicate that strength has increased, without attendent loss of ductility, with increasing exposure time. This apparent strengthening effect cannot be explained at this date.

Pratt & Whitney Aircraft, Canel[201, 274]. Several relatively successful coatings specific to certain columbium alloys have been developed at Canel. These coatings are applied either by hot-dipping in an aluminum-base alloy followed by appropriate heat treatment to produce mixed intermetallic compounds such as $CbAl_3$, $CbSi_2$, and $CbCr_2$, or by pack vapor-diffusion treatments in which complex silicides, chromides and borides of molybdenum, columbium, and titanium are formed in the surface layers of the specimen.

The wide divergence of the various columbium alloys in chemical and metallurgical properties often requires additional exploratory work before a coating developed for a particular columbium composition can be successfully applied to specimens of a different columbium alloy. Experimental coatings are screened by oxidation testing in stagnant furnace air at elevated temperature. Successful coatings are then further evaluated over a broad temperature spectrum in flowing air by resistance heating with thrice-daily thermal cycling to room temperature. The ability of a coating to deform at service temperature without loss of its protective properties is determined by performing stress-rupture studies on coated specimens in air furnaces. The effects of various rates and degrees of cold deformation on protectivity at high temperature are subsequently measured. Approximate impact and erosion resistance may be inferred from these tests, but more exact measurements are necessary.

In hot-dip coating columbium alloys, prior conditioning of the specimen surface is important at dipping temperatures of less than 1650 F or if no flux is employed, but melt temperatures above 1800 F permit increased pretreatment flexibility. Immersion times vary with the melt temperature and the substrate composition: columbium-20 weight per cent titanium alloy achieves the desired coating thickness of 2 mils in less than 15 seconds when dipped in aluminum-10 weight per cent chromium alloy at 1900 F, while unalloyed columbium requires 10 minute. t 1700 F and 2 minutes at 1900 F in the same

melt. Posttreatment of hot-dipped aluminum-base coatings is an important aspect of the method. Apparently, any kind of thermal treatment in the absence of air at temperatures in the range 1600 to 1900 F improves hot-dip coating performance, but vacuum firing at 1900 F or pack calorizing at 1800 F are superior to heat treatment in inert gas. The high degree of elevated temperature ductility of aluminum-base hot-dip coatings on columbium-20 weight per cent titanium alloy has been demonstrated during stress-rupture tests conducted in air. Present data are inconclusive as to the extent of cold deformation permissible on parts that are to be subsequently heated in air. Impact and erosion resistance have not been quantitatively measured but it is anticipated that the former will be fair, considering the moderate self-healing character of this coating-substrate combination, and that the latter will be good in air but poor under highly abrasive conditions. Coated columbium-20 weight per cent titanium rods self-resistance heated in flowing air appear to be relatively insensitive to moderate thermal cycling and do not demonstrate the catastrophic failure in the 1100 to 1400 F zone that is characteristic of the intermetallic compound $CbAl_3$.

Specimen preparation for the pack vapor-diffusion process consists of relieving sharp edges and pickling in mixed acids. Two-to-three-mil coatings are produced on most columbium-base compositions by firing in a mixture of several metals of the group molybdenum, titanium, silicon, chromium, boron, tantalum, beryllium, gadolinium, and tin dispersed in an inert metal oxide together with a small quantity of accelerator such as iodine for up to 24 hours at 2100 F. The process is flexible in all particulars except accelerator concentration and firing temperature. No posttreatment is specified for pack-coated parts. Earlier work involving binary systems from the group of elements given above indicated that some coating-substrate combinations were subject to the catastrophic low-temperature failure previously described, but this condition was alleviated by adopting ternary and higher mixtures and by introducing the idea of successive pack firing in different binary compositions. Being constituted almost entirely of intermetallic compounds, most of these coatings demonstrate room-temperature hardnesses in the range 1200 to 1900 DPH and, for this reason, might not be expected to withstand strain except at very high temperatures. Stress-rupture tests performed in air have shown, however, that considerable deformation is permitted if the strain rate is sufficiently slow. On the basis of observed hardnesses, impact resistance should be marginal while erosion resistance both to air and abrasive particles should be fairly high. A degree of self-healing has been encountered in certain coating-substrate combinations and efforts are being made to relate this property to specific material ingredients and concentrations.

Sylvania Corning Nuclear Corp. Considerable work has been done at Sylcor on the protection of columbium-base alloys from oxidation. Most of the information is classified. Hot dipping in an aluminide-base bath followed by a diffusion anneal is a procedure which has been used extensively.

Information on one coating, designated G-14, has been made available. This coating is applied by dipping in a molten Al-5Cr-5Ti bath at 1900 F, followed by a 1-hour diffusion anneal at 1900 F in an Al_2O_3-Al pack under argon, which produces $CbAl_3$ plus unknown phases in the coatings.

Protection of the following substrates under the indicated conditions has been reported:

Substrate	Temp, F[a]	Total Time, hr	Number of Cycles	Stress, psi	Elongation, %
Cb-15W-5Mo-1Zr	2500	10	10	500	1.5
Cb-5Hf-1Ti-1Zr	2600	10	10	400	3

(a) Resistance heating with simultaneous shut-off of current and opening of air blast every hour.

The oxidation rate at 1400 F has been reported to be relatively high, but protection is provided for over 10 hours.

Zinc-Base Coatings. [269-272] The first reports in 1959 that workers at the Naval Research Laboratory had discovered that zinc would protect columbium from oxidation caused much interest in this coating. Although it was found that the maximun use temperature of zinc-coated columbium is about 2050 F, and therefore is of little interest for gas-turbine and space-vehicle applications but may find some use in AEC applications, the coating system exhibits some unique characteristics.

It is not possible within the scope of this report to do complete justice to the outstanding scientific thoroughness with which the many coordinated efforts at the Naval Research Laboratory investigated zinc-columbium base systems; these efforts and results have been reported in detail elsewhere, [270-272] and a DMIC Memorandum summarized the findings [269]. Selected features of this work are presented here.

Fundamental Properties of the Cb-Zn System. Figure 56 shows the columbium-zinc phase diagram. Four intermetallics are present in the system: CbZn, $CbZn_{1.5}$, $CbZn_2$, and $CbZn_3$, which is the major phase formed when columbium is coated with zinc. These intermetallics decompose by peritectic reactions, the temperatures of which were determined by observations on Cb-Zn alloys encapsulated in silica, and thus represent equilibrium temperatures under a pressure of 6 to 8 atmospheres of zinc vapor.
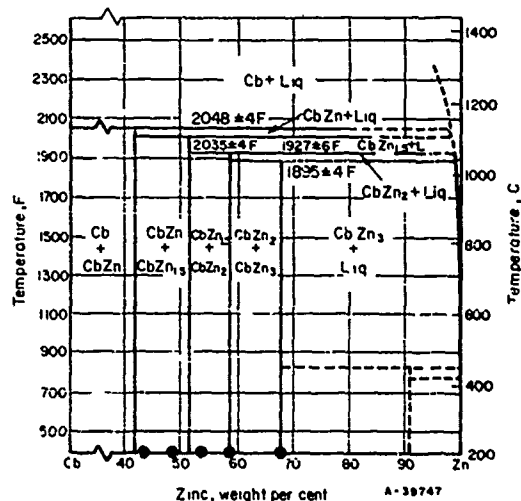
FIGURE 56   COLUMBIUM-ZINC PHASE DIAGRAM [270]
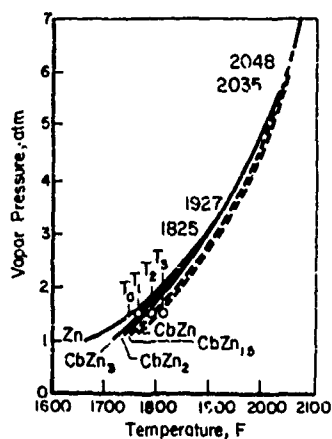
FIGURE 57. VAPOR-PRESSURE CURVES FOR ZINC AND COLUMBIUM-ZINC
INTERMFTALLIC COMPOUNDS (SCHEMATIC)[270]
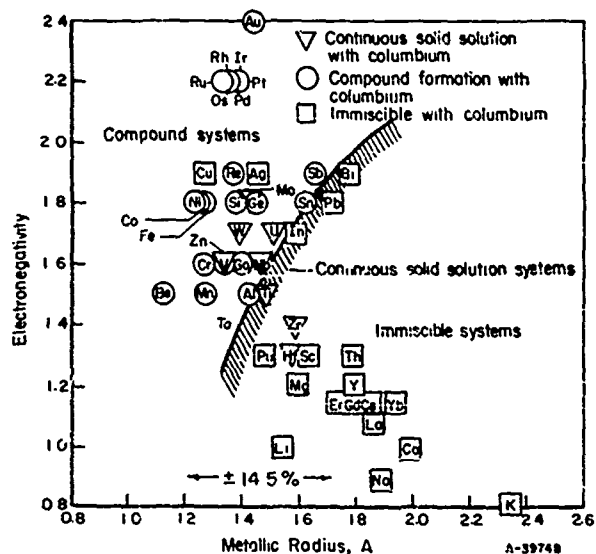
FIGURE 58. A HUME-ROTHERY PLOT FOR BINARY COLUMBIUM ALLOYS[270]

(Both electronegativities and metallic radii are from Pauling.)

Vapor pressure curves for zinc and Cb-Zn intermetallics are presented in Figure 57. The position of zinc in a Hume-Rothery plot for binary columbium alloys is shown in Figure 58.

Figure 59 shows liquidus-solidus lines for the system Cb_2O_5-ZnO which becomes of interest in an oxidizing atmosphere. The effects of oxide additions have been investigated qualitatively. It appears that several oxides, including those of copper, iron, and nickel, lower the melting points in the Cb_2O_5-ZnO system.
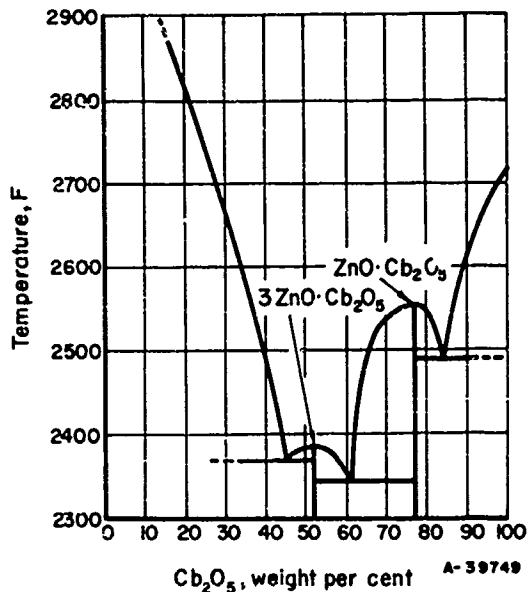
FIGURE 59. LIQUIDUS AND SOLIDUS LINES FOR THE SYSTEM ZnO-Nb$_2$O$_5$[270]

Preparation of the Zinc-Base Coating. Zinc coatings may be applied to columbium by several different procedures:

(1) Vapor distillation of zinc onto columbium

(2) Hot dipping of columbium in molten zinc with a subsequent interdiffusion treatment

(3) Aqueous electroplating of columbium with zinc followed by an inter-diffusion treatment

(4) Cladding of columbium with zinc followed by an interdiffusion treatment.

Hot dipping has been found advantageous for making ternary or higher additions to the coating system.

Vapor distillation of zinc on columbium using evacuated silica capsules has been studied in detail. The growth of $CbZn_3$ on columbium with time is shown in Figures 60 and 61; the growth as a function of temperature is given in Figure 62.
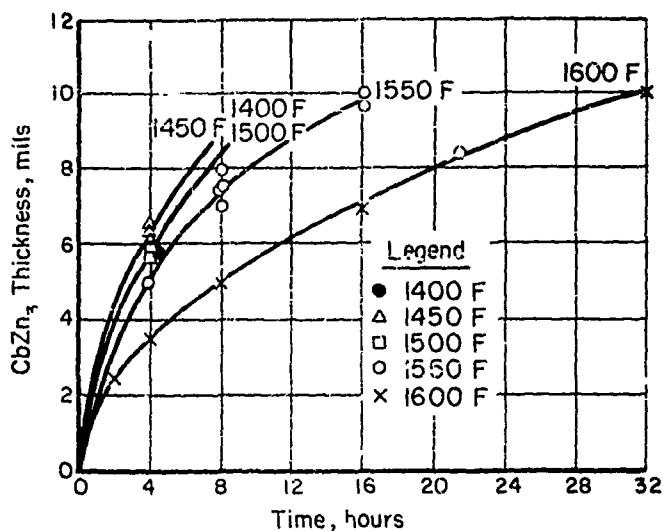
FIGURE 60. GROWTH CURVES OF CbZn₃ ON COLUMBIUM FROM THE VAPOR
AT SEVERAL TEMPERATURES[270]
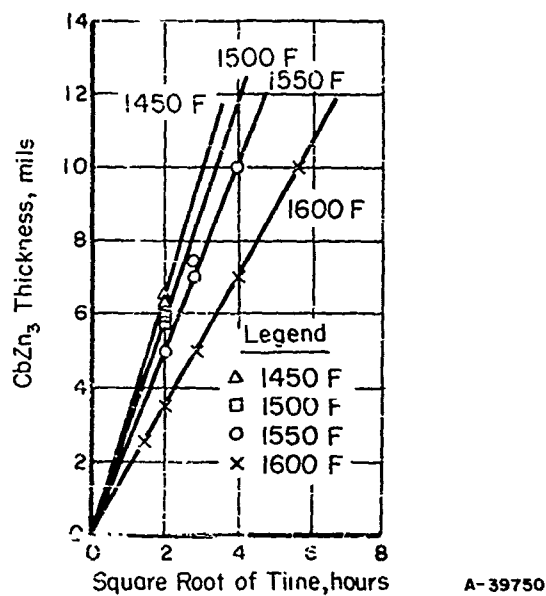
FIGURE 61. GROWTH CURVES OF CbZn₃ ON COLUMBIUM FROM THE VAPOR
AT SEVERAL TEMPERATURES, PLOTTED AGAINST THE
SQUARE ROOT OF TIME[270]

The straight lines demonstrate a parabolic rate of growth, and
therefore diffusion control.
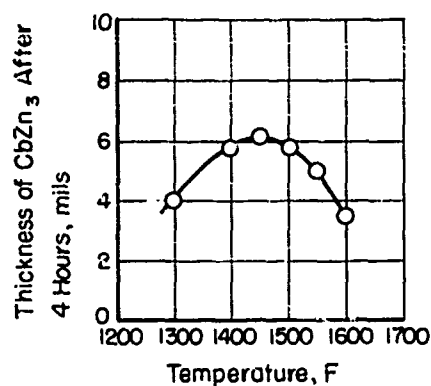
FIGURE 62. THE THICKNESS OF CbZn₃ FORMED FROM THE VAPOR
IN 4 HOURS AS A FUNCTION OF TEMPERATURE[270]

Performance Characteristics. The transformations which occur in zinc-coated columbium as a function of time in air at 1600 and 1800 F are shown in Figures 63 and 64, respectively.
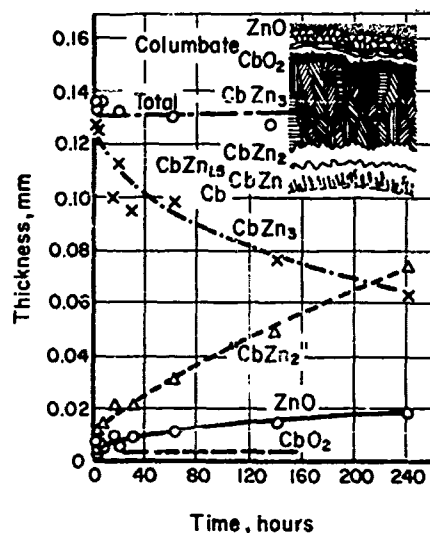
FIGURE 63. AIR OXIDATION OF Zn-Cb   FIGURE 64. AIR OXIDATION OF Zn-Cb
COATING AT 1600 F[270]   COATING AT 1800 F[270]

ZnO spire form 'tion (Figure 65) becomes a problem at 1800 F and above because of the high vapor pressure of zinc. This problem may be reduced by "conditioning" the coating system in air at 1600 F or higher in stages to form a more rigid pressure-containing

envelope of ZnO and increase the amount of the more stable $CbZn_2$ in the coating. The conditioning procedure can vary depending on the desired service temperature, as indicated for the data represented in Figure 66.

FIGURE 65. GROWTH OF SPIRE OF ZnO FROM A TAB OF COLUMBIUM COATED WITH ZINC AND DIFFUSED, EXPOSED TO STAGNANT AIR AT 1800 F[270]

Numerous tests were run in flowing combustion products on zinc-coated columbium and Cb-1Zr at the Naval Aeronautical Engine Laboratory.[270] The more important conclusions drawn from the tests were:

(1) The coating performed about as well in high velocity (up to 2480 feet per second for 5 hours at up to about 2100 F) as it did in stagnant air.

(2) There were no apparent effects of combustion-gas velocity on the performance of the coating.

(3) The temperature limit of the coating was around 2100 F (for 5-hour periods) in burned propane and JP-4. In burned hydrogen the limit may be somewhat lower (~1900 F). The temperature limit of coated Cb-1Zr may be slightly lower than that of coated columbium.

(4) Deposits of carbon and/or impregnated asbestos gasketing may cause the coating to fail.

The most remarkable quality of the zinc-base coating on columbium has been its ability to repair relatively large defects in itself This self-healing ability is believed associated with the relatively high zinc vapor pressure over the columbium-zinc intermetallic compounds. When a defect occurs, the underlying columbium immediately begins to oxidize to Cb_2O_5. This oxide is rapidly permeated by zinc vapor from the adjacent columbium-zinc compounds (within 10 to 30 minutes at 1800 F). The zinc then oxidizes, forming a protective ZnO layer at the Cb_2O_5-air interface, arresting the columbium oxidation reaction The repair action is completed when the zinc vapor reacts with the underlying columbium metal to form a layer of the lower intermetallics. This layer serves as a zinc reservoir for the protective outer ZnO scale.

The repair action of zinc coatings is shown in Figure 67. The upper sketch shows a 1/2 x 3/4-inch coated specimen from which was milled a 3/8-inch-wide area; all of the Cb-Zn compounds were thus removed from this area. The bottom photo shows the microstructure of this defected are after exposure for 20 hours at 1800 F in air.
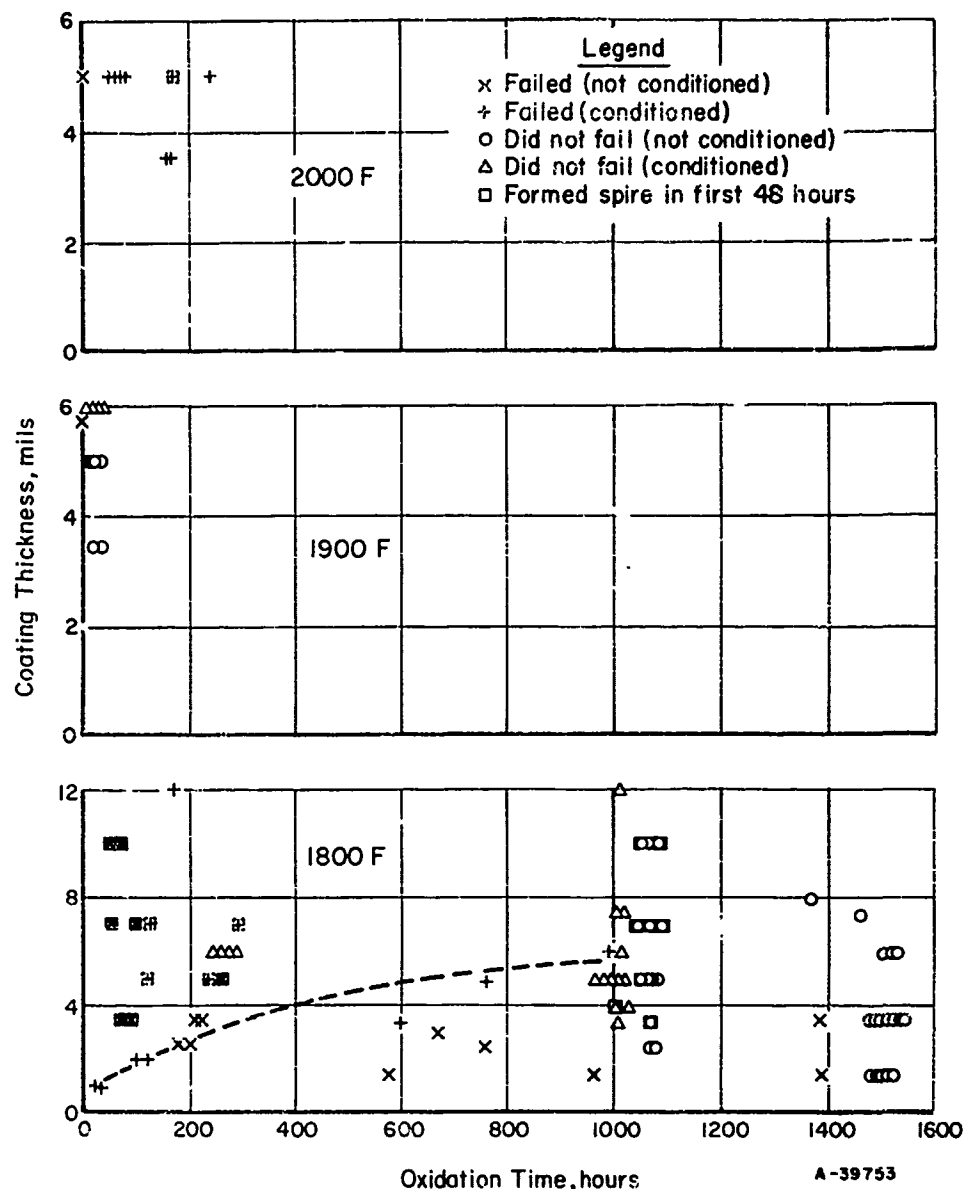
FIGURE 66. AIR OXIDATION AT 1800, 1900, AND 2000 F OF ZINC-COATED COLUMBIUM[269]

Coatings were applied by vacuum distillation at 1600 F for samples exposed at 1800 F, and at 1900 to 2000 F for samples exposed at 1900 F and 2000 F. Samples exposed at 1800 F were conditioned ₃ hours at 1600 F; samples exposed at 1900 and 2000 F were conditioned 24 hours at 1600 F plus 24 hours at 1800 F.
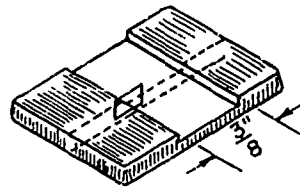
a. Slotted Specimen   A-39754

a. Slotted Specimen

ZnO

Cb$_2$O$_5$

CbO$_2$

CbZn$_x$

b. Microstructure of Defected Area After
20 Hours at 1300 F in Air

FIGURE 67.   SKETCH OF DEFECTED Zn-COATED COLUMBIUM AND
MICROSTRUCTURE OF REPAIRED DEFECT AFTER
AIR EXPOSURE(270)

The temperature range in which gross flaws are healed is limited to that in which the vapor pressure of zinc is relatively high. Tests made at 700, 1000, and 1300 F showed that detects such as cut ends are not healed at low temperature; however, flaws or cracks produced by thermal cycling are healed. At 1800 F specimens which have been bent or cut in half healed rapidly on exposure.

The upper limit for self-healing is estimated as 2048 F, the temperature .t which CbZn decomposes in the coated system.

As would be expected for a self-healing coating, oxidation resistance of coated specimens has been good within the temperature range of self-healing under cyclic and impact testing.

Several pure columbium metal strips 0.050 by 0.50 by 2.75 inches were coated by NRL and evaluated by the General Electric Company, FPLD.[171] The coating procedure consisted of immersing the columbium specimens in molten zinc at 1025 F for 2 hours and heat treating in air at 1600 and 1775 F for periods of 20 and 1 hours, respectively. The coated flat specimens were exposed by GE to 50 thermal-shock cycles between 1000 to 2000 to 1000 F for a total time of 35 minutes at a gas velocity of 45 feet per second. At 2000 F, the coating appeared to contain a great amount of liquid phase. No hardness increase was detected at all in these tests, even within 3 mils of the zinc-columbium intermetallic layer. Conclusions reached in the GE evaluation under the conditions of the tests were as follows:

(1) Zinc-coated columbium will survive at least 50 cycles, and no doubt more, to 2000 F with no significant metal contamination.

(2 This coating showed limited life at 2000 F, and no useful oxidation resistance at 2300 F.

(3) The zinc coating on columbium offers unusual self-healing characteristics.

The effects of alloy additions to the zinc coatings have been studied. Additions evaluated include aluminum (8 to 75 per cent), cobalt (1 per cent), copper (20 per cent), chromium (0.5 to 1 per cent), iron (1 per cent), magnesium (0.5 to 20 per cent), silicon (0.5 per cent), titanium (3 to 10 per cent), and zirconium (3 to 10 per cent). The coatings were applied to columbium by hot dipping in the range 1000 to 1600 F, followed by conditioning at 1600 F in air for 16 hours.

Aluminum, titanium, and zirconium were the only additions showing improvements over the unalloyed zinc coating, and these improvements were mainly in the reliability in the 1800 to 2000 F range.

Aluminum additions progressively raised the upper temperature limit for exposure without early failure. The coating life at temperatures below 2000 F was slightly reduced, however, and aluminum also reduced the self-healing properties. Coatings containing more than 15 per cent aluminum were not self-healing. A coating of Zn-10 per cent Al appeared to offer the best compromise. Coatings of this composition have withstood 20 hours at 2200 F.

Titanium additions in the range 4 to 6 per cent appeared beneficial in reducing the tendency to form spires at 1800 F. These coatings had good life at 1800 F, but showed

no improvement over the straight zinc coating at 2000 F. A ternary addition of 0.5 per cent aluminum to the bath reduces contamination hardening during subsequent exposure. An increase in titanium content to 10 per cent reduces the coating life. Zirconium additions to the bath produce effects similarly to those produced by titanium.

Zinc coatings were applied by hot dipping to binary columbium alloys containing aluminum (1 and 2 per cent), iron (1 to 8 per cent), molybdenum (3 per cent), titanium (5 to 20 per cent), tungsten (7 and 10 per cent), vanadium (3 to 7 per cent), and zirconium (1 to 7 per cent). Zinc coatings were applied similarly to the following complex alloys:

Cb-40Ta-10Ti
Cb-30Ta-0.07Zr
Cb-10Ti-10Mo
Cb-40Ti-5Al-5Cr
Cb-15W-5Mo-1Zr.

All of these zinc-coated alloys behave similarly to zinc-coated columbium.

Zinc coatings could not be formed on unalloyed tantalum, molybdenum, or tungsten. Some success was obtained on vanadium, as will be described later.

Oxide-Base Coatings

Oxide-base coatings applied by spraying techniques generally have been porous and have not given significant protection. It appears that these coatings require an impregnation with another material to be operable.

A notable case where this has been done, and also a case which represents some designing of a coating system and an analysis of the factors involved, is that of the General Electric System 400, which has been reported by Hall and Graham[61]. This coating consists of flame-sprayed alumina impregnated with a baria-alumina-silicate glass sealant. The oxide coating approach was chosen because of its potential refractoriness and chemical stability with columbium. Further, the known procedures used for enamel-coating development appeared to be applicable for producing desired thermal expansion, composition, and maturing requirements in the 2000 to 2600 F temperature range.

An outline of the coating-system preparation procedure is as follows:

(1) The columbium specimen is grit blasted to improve adherence of the flame-sprayed alumina.

(2) Specimen is vapor blasted to clean surface.

(3) Flame-sprayed alumina is applied.

(4) Glass slurry is applied.

(5) Slurry is dried.

(6) Slurry is fired in protective atmosphere at 2700 F to seal.
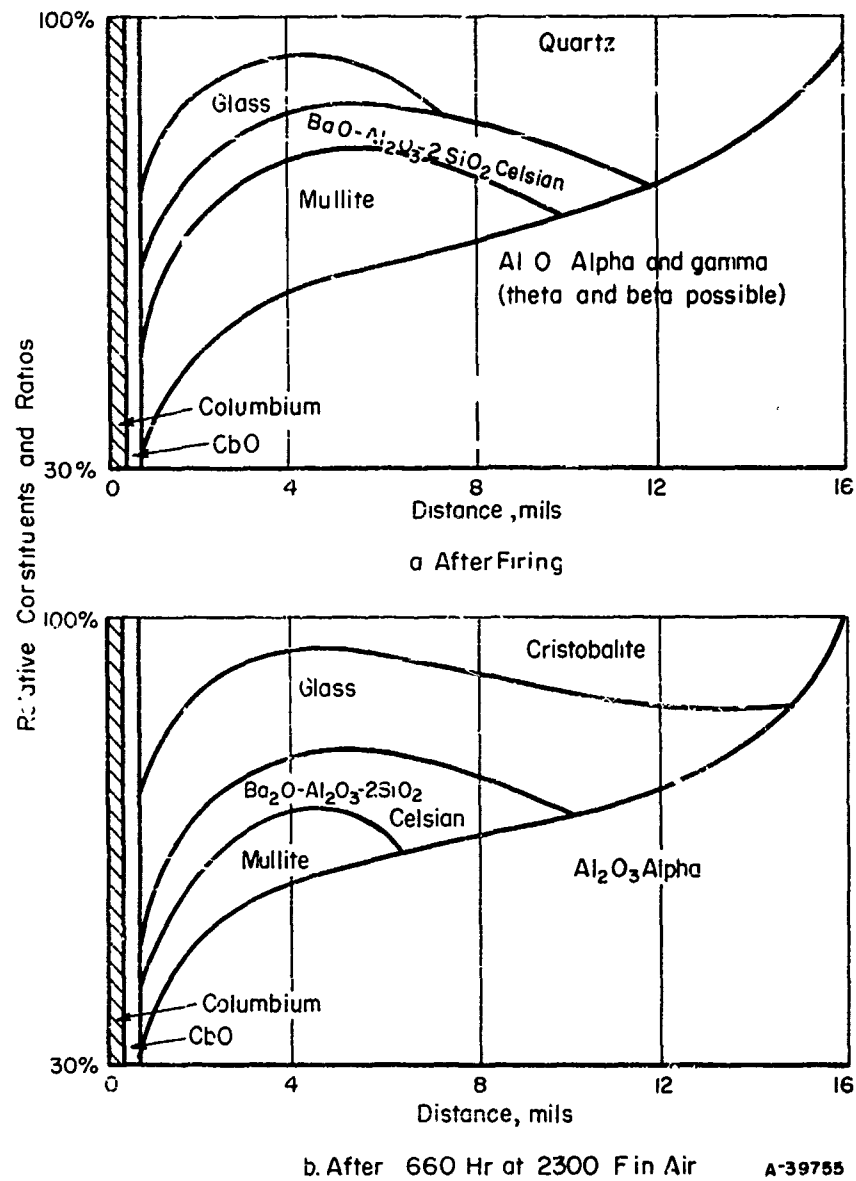
FIGURE 68. COMPOSITION OF SYSTEM 400 BY QUALITATIVE X-RAY ANALYSIS[61]

Figure 68 shows the qualitative chemistry of System 400 on columbium as prepared and after 660 hours in air at 2300 F.

The bonding between System 400 and the columbium substrate is excellent, and is believed to be chemical in nature. X-ray diffraction analysis of this system indicates that there is a layer of CbO between the columbium and the ceramic coating. Figure 69 is a graphical representation of the calculated expitaxial fit and orientation between CbO and columbium. Because of the unit cell size of columbium (bcc, d = 4.6 A) and CbO (cubic, d = 4.21 A), a better fit is obtained by the diagonal placement of CbO over the columbium. There is some question as to the abnormal stability of the metastable CbO at 2300 F. This compound is believed to remain stable because of the energy levels established between the oxide and the metal which should effect the transformation equilibrium. In addition, the CbO phase must always exist between columbium and its higher oxides. X-ray diffraction analysis tends to substantiate a theory that, as the CbO oxidizes to the higher valence state, the higher valence oxides are dissolved by the System 400 coating oxides; Cb_2O_5 then precipitates from solution upon cooling.

CbO lattice

Cb lattice
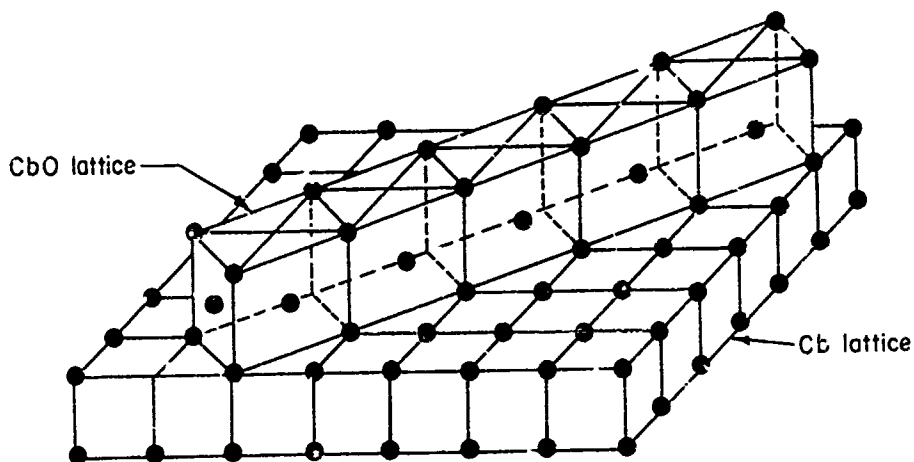
Bond — Chemical (ionic)
Crystal Fit — within 15 per cent per Goldschmidt's Law
Thermodynamic Properties — Stable due to bond
Diffusion Properties — barrier to oxygen
Mechanical — Good stress gradient of system 400 to Cb

FIGURE 69. EPITAXY OF CbO ON Cb[61]

Thermal-stress measurements were also made of the System 400 coating on columbium. The stresses were calculated from strain measurements of heated cantilever specimens. These measurements were done in non-oxidizing atmospheres. Stress calculations were made using measured elasticity values of sprayed and heat-treated Al_2O_3, and some estimated modulus values of the composite system. As shown in Figure 70, the stress level of System 400 coating decreases from about 15,000 psi tensile at 70 F to 0 psi at 1600 F. This reduction is caused by the differential in thermal coefficient of expansion of the coating and columbium. The stress is definitely not relieved by viscous flow since the coating is not soft at even 1700 F, as determined by impact tests. The increase in the stress level of System 400 over flame-sprayed

alumina is believed to be due to two phenomena. The first is the increase of modulus of elasticity from 1.5 to 45 million psi of the heat-treated alumina as compared with sprayed alumina. This has been discussed elsewhere[61]. The Al_2O_3 phase is between 80 and 90 per cent of the entire coating volume and should, therefore, contribute most significantly to the resultant stress of the entire oxide system. The second phenomenon is the related stresses that are produced by the formation of new phases precipitating from the high-temperature glass-alumina system upon cooling. No measurements have been made of volume changes which could cause stress to increase from zero at 1700 F to 15,000 psi at 70 F.

The thermal-expansion coefficients of the System 400 constituents are shown in Figure 71; they are all approximately of the same magnitude, with columbium having a slightly higher coefficient than System 400. This would normally indicate that the coating would be under compressive stress after processing. However, as indicated above, the coating is under tensile stress caused by the inherent stresses resulting from flame spraying Al_2O_3.

Unalloyed columbium and F-48, F-50, FS-80, and FS-82 columbium alloys have been successfully protected. Comprehensive test results of System 400 coating on pure columbium are as follows:

Static-Oxidation Testing Life[a]

Test Temp, F	Nominal Life, hours	Maximum Life Obtained, hours
2300	500	1400
2500	100	--

Thermal Shock 1000 F-2300 F-1000 F — 2-Minute Cycle

Nominal Life, cycles	Maximum Life, cycles
500	1000

Flexure — 180-Mil Deflection With Thermal Cycles as Above

Nominal Life	Maximum Life
1.0×10^6	1.5×10^6

(a) As pertains to oxide growth failure only.

Impact testing was done with a nitrogen-pressurized air rifle shooting a 1/16-inch stainless steel pellet that was traveling at 750 feet per second at the instant of impact. The results showed that the coating was brittle at 1700 F, plastic at 2300 F, and mushy at 2500 F.

A screening test was developed to establish the reliability of any given System 400 coating. After coating, the piece was subjected to a 10-hour static oxidation test at 2300 F. On the basis of a large number of samples, if a coated piece did not show signs of failure in 10 hours it would last for a minimum of 500 hours at this temperature. Since the flame-sprayed aluminum oxide by itself affords no protection to the columbium substrate, regions which are not adequately impregnated by the glass sealant fail in a
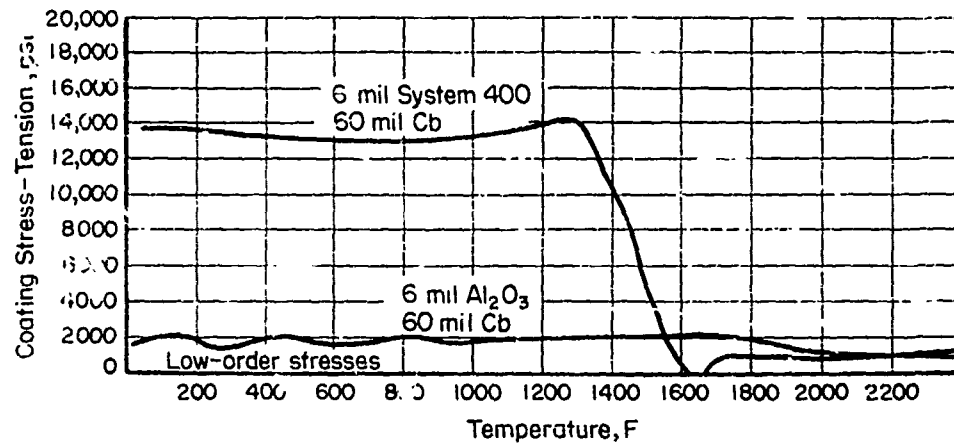
FIGURE 70. APPARENT RESIDUAL STRESS DEVELOPMENT IN FLAME-SPRAYED
ALUMINA ON COLUMBIUM-SYSTEM 400[61]
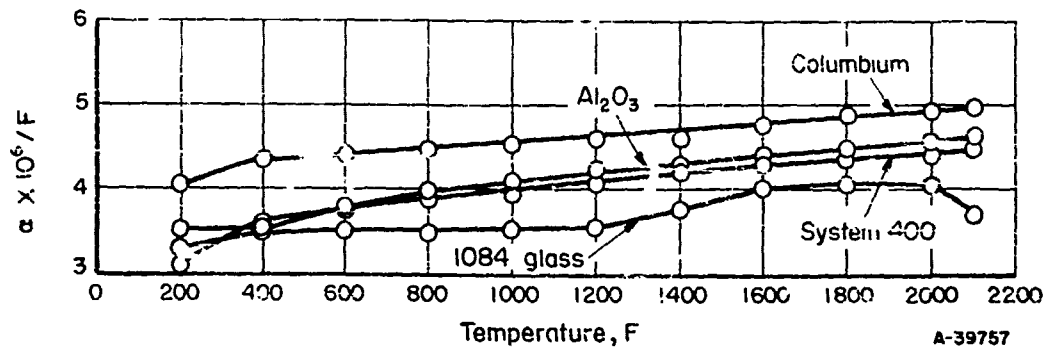
FIGURE 71 THERMAL-EXPANSION COEFFICIENTS OF CONSTITUENTS
IN SYSTEM 400[61]

very short time. Therefore, the short-time oxidation test allows for quite reliable inspection of a coated piece.

The System 400 coating has been applied with good results to single specimens and complex shapes.

It has the following limitations:

(1) The object being coated must have exposed surfaces capable of being flame sprayed.

(2) The processing temperature is high (2700 F); some adjustment downward may be possible.

(3) Application to thin sheets (10 to 20 mil) has not been possible without contamination.

(4) Under impact conditions in the range of brittleness the coating may not be protective.*

Unclassifiable Coatings

According to Withers[226c], the following results were obtained at the American Machine and Foundry Co. for diffusion-coated columbium processed by pack cementation:

Coating	Protective Life at 2500 F, hr
Amfkote-3	396
Amfkote-4	34

These coatings are reported to be less resistant to thermal shock than Amfkote-2, which was discussed under coatings for molybdenum. Amfkote-4 has been reported to have self-healing characteristics.

Comparative-Evaluation Program on Coating Systems

As a part of its Air Force sponsored program on protective coatings for columbium, Thompson Ramo Wooldridge[201] has been conducting a comparative-evaluation program. Results from this program have not as yet become available.

Three substrates and six coatings are involved in the program. The substrates are:

(1) Unalloyed columbium

(2) F-48

(3) D-31.

*Brittleness at the lower temperatures is common in most coating systems.

The six coatings, which were applied to the substrates by their respective vendors, are:

Vendor	Coating
Chromalloy Corporation	Modified W-2
Chromizing Corporation	Durak Cb
General Electric Co., FPLD	LB-2 (hot dipped or slurry dipped aluminide)
Sylvania Corning Nuclear Corp.	Sylcor Coating (hot dipped aluminide)
Thompson Ramo Wooldridge Inc.	TRW, Cr-Ti-Si
Vought Astronautics	Multicycle pack-cementation coating

Comparative evaluation of the six coatings on the three different substrates is being done by the following tests, the details of which will be published elsewhere: [201]

(1) Cyclic oxidation

(2) Thermal shock-erosion oxidation

(3) Bend ductility

(4) Tensile-stress oxidation.

COATINGS FOR TANTALUM

Coatings for Tantalum

Major research on protective coatings for tantalum-base alloys has been in progress for only about a year and a half; however, significant results have been achieved. Coating types and techniques previously used for columbium have, in some cases, been used to good advantage on tantalum.

Aluminide-Base Coatings

Aluminum forms the oxidation-resistant MAl3 with tantalum as it does with columbium. Numerous modifications of the pure TaAl3 have been explored and some have been found to make a much better coating than TaAl3.

Metals and Controls (Texas Instruments).[277] Roll cladding of aluminum and aluminum-base alloys to tantalum followed by a diffusion-reacting anneal to form the intermetallic coating has been under investigation at Metals and Controls*. High purity aluminum, 2S aluminum, and Al-12Si have been used for claddings for subsequent reaction with the substrate at 1500 to 1800 F for 1 hour in argon. Preliminary results indicate that the procedure may have merit, but considerable development work is necessary to permit comparison of the coated products with the current state of the art. Edge protection may be a problem.

An extension of this work to form a multilayered tantalum-aluminide coating composite also has been briefly explored for possibilities of forming a self-healing coating.

An aerospace company has been reported to be evaluating products formed by these methods.

Sylvania Corning Nuclear Corporation.[209, 210] An extensive Air Force sponsored program has been in progress at Sylcor to evaluate aluminide-base coatings on tantalum alloys**. Reference should be made to the final report on this work, which is in preparation, for a full account of the research carried out by Sama and his associates.

Coatings have been applied in several ways: (1) hot dipping in pure aluminum and various aluminum alloys followed by a diffusion treatment, (2) hot dipping in tin base-aluminum alloys, (3) painting or spraying with lacquer suspensions of metal powder and diffusing, and (4) pack cementation in mixed powders. Dipping temperatures were in the range of 1700 to 1900 F. In all nonpack processes, initial coating was usually followed by a diffusion anneal at 1900 F. However, Sn-Al dipped samples usually were tested as dipped. Pack cementation was done at 1900 F for several hours. In all cases, times and temperatures were adjusted to give approximately 2-mil-thick coatings.

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* Exploratory work has been done with molybdenum and columbium substrates also.
** Work on beryllide coatings done at Sylcor will be presented in the next section.

Evaluations have been made using furnace, self-resistance, and oxyacetylene torch heating, under isothermal and cyclic conditions, and with and without tensile stress. Five important aspects of evaluation procedures should be noted from the overall program:

(1) Differences in performance have been observed between furnace heating and self-resistance heating.

(2) It was found in self-resistance heating that performance can be a function of the type of current used, ac or dc. A "knuckle" of material frequently formed at the negative electrode with direct current, causing premature failure.

(3) Tests conducted at 2500 to 3000 F on Sn-Al coated samples with an oxyacetylene torch under oxidizing conditions gave results which were similar to those obtained with furnace heating, although lives were somewhat shorter.

(4) In general it was observed that all coating compositions investigated had materially shortened lives in cyclic exposure testing.

(5) Several aluminide-base coating compositions on tantalum have exhibited shorter lives at lower temperatures ($\sim$1400 F) than they have at the higher temperatures, as was similarly indicated earlier for aluminide-base coatings on columbium.

The most promising coating to date appears to be a 2-cycle spray, diffusion-spray, diffusion coating utilizing a composition of 50Al-50Sn; the coating produced by this technique has been designated 34S. Most of the results for this coating have been obtained using a Ta-10W alloy; little difference has been noted between unalloyed tantalum and Ta-10W with aluminide-base coatings. Oxidation life of 34S coated Ta-10W is shown in Figure 72. Thermal cycling accelerated oxidation as shown by Figure 73.

A remarkable feature of the coating formed from the 50Al-50Sn composition is its ability to tolerate an abundance of physical abuse prior to oxidation without any decrease in subsequent protectiveness. Samples have performed well after receiving Vickers hardness impressions, bending 90 degrees over a 2T radius, and twisting 360 degrees. One sample was literally tied into a knot. None of these samples showed accelerated attack at 2600 F for 10 hours. Apparently, after diffusion treatment at 1900 F during preparation, the coating consists essentially of $TaAl_3$, but there is enough unreacted Sn-Al to give a residual liquid phase at elevated temperatures which permits healing of defects.

On exposure at temperatures above 1900 F, the $TaAl_3$ interdiffuses rapidly with the substrate and quickly converts to lower aluminides. For protection against oxidation, it is essential that an oxide film be formed on the surface before this rapid interdiffusion occurs to the extent that most of the $TaAl_3$ phase is converted to Ta_2Al.

The upper temperature limit of the 50Al-50Sn coating, which would be time dependent, is thought to be in the range of 3000 to 3600 F.
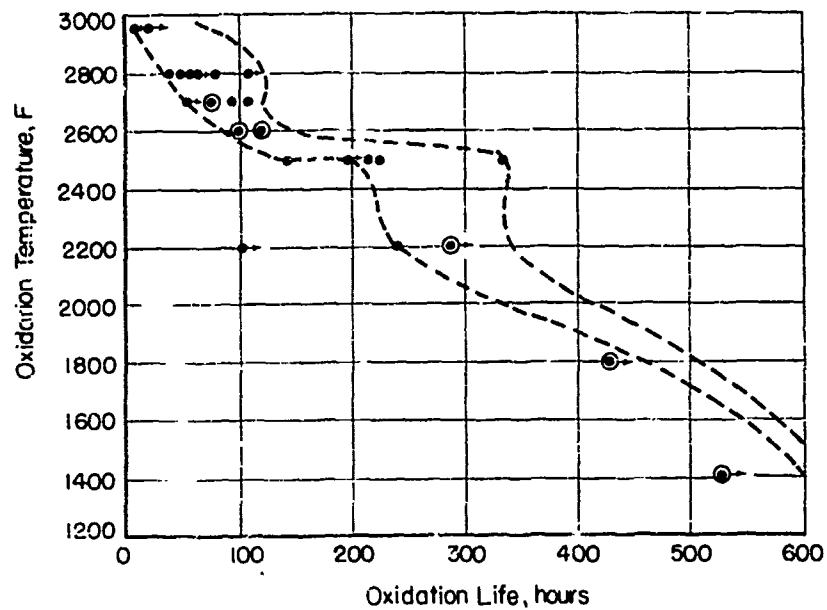
FIGURE 72. OXIDATION LIFE OF 34S COATED Ta-10 W ALLOY SAMPLES [210]
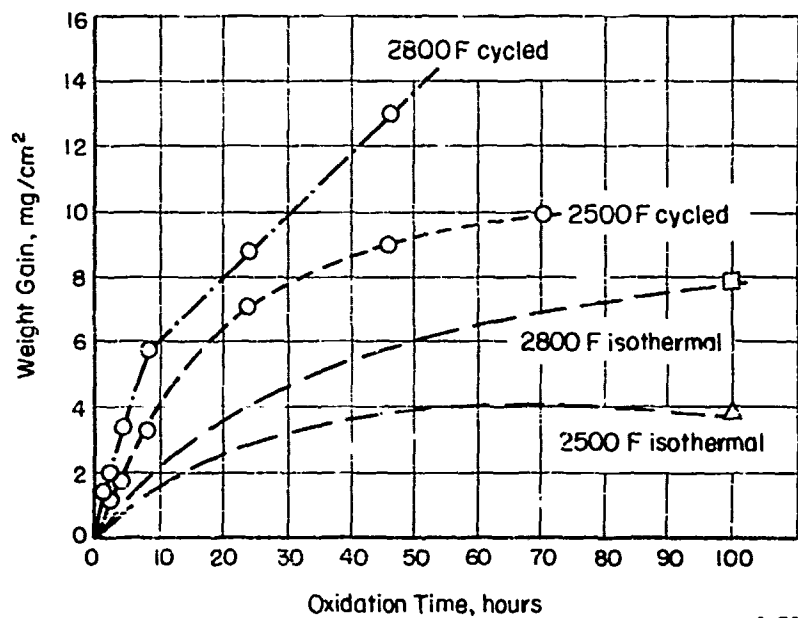
A-39758

FIGURE 73. WEIGHT GAINS OF 34S COATED Ta-10 W SAMPLES OXIDIZED AT 2500 AND 2800 F [210]

It was recently reported by Rosenbery[226c] that 50Al-50Sn coated Ta-1CW with-stood 5 minutes in an arc plasma jet at 3340 F. Thermal cycling (20 seconds of heating, 20 seconds of cooling) produced failure at about 2900 F in five of six tests.*

Beryllide-Base Coatings

In conjunction with its extensive studies of aluminide coatings on tantalum, Sylcor also investigated beryllide coatings. These were formed by a vapor-solid reaction technique in a vacuum furnace at 1800 to 2200 F for from 2 to 25 hours. Samples were placed between sheets of beryllium rolled from powder. The relatively high vapor pressure of beryllium at the temperatures used and its rapid reaction with the tantalum samples readily provided uniform 2-mil coatings.

Beryllide coatings on tantalum were found to resist oxidation for 10 hours at 2500 F in both cyclic and isothermal exposure. However, samples stressed during exposure failed quickly. The coatings were much superior on Ta-10W. Beryllide coatings on this alloy gave protection at 2500 to 2700 F for 10 hours and 10 cycles under stresses producing 1 to 15 per cent elongation. At 2800 F, mixed results were obtained, but for the most part, samples lasted less than 5 hours. Isothermally exposed samples lasted much longer at all temperatures than did cycled samples.

Somewhat anomalous behavior was noted at lower temperatures. Many relatively early failures occurred, especially at 2200 F. However, some samples lasted for 64 hours or more without failure.

Diffusion effects on substrate thickness are shown in Figure 14. Rapid diffusion was observed between the $TaBe_{12}$ coating and tantalum substrate at 2500 F and higher; substrate thickness decreased from about 9 mils to 2 mils in 15 hours at 2500 F. Diffusion occurred much less rapidly in beryllide-coated Ta-10W, as shown in Figure 14. This can be contrasted with the aluminide system where little difference was observed in diffusion rates between tantalum and Ta-10W substrates.

Silicide-Base Coatings

As with columbium, silicide-base coatings on tantalum have shown promise for providing significant protection. To date these coatings have been applied by vapor deposition using either the pack-cementation technique or deposition from a continuous gaseous phase.

Battelle Memorial Institute. [45,190] In a program sponsored by the Air Force, and parallel to that conducted at Sylcor, several coating compositions have been under study at Battelle for tantalum-base substrates. Aluminide and beryllide coatings were excluded from the program by Air Force agreement due to the work being done at Sylcor.

* Preliminary results reported by Rosenbery indicated that this coating may also have some promise for protecting tungsten, molybdenum, and columbium.

500X   N77602

FIGURE 74. MICROSTRUCTURE OF SILICIDE-COATED TANTALUM EXPOSED IN
            AIR FOR 3.3 HOURS AT 2500 F[190]

            Initial coating thickness, 2.5 mils.

500X   N77032

FIGURE 75. MICROSTRUCTURE OF SILICIDE-COATED Ta-30Cb-16V ALLOY AFTER EXPOSURE IN
            AIR FOR 7 HOURS AT 2700 F (NO FAILURE)[190]

            Initial coating thickness, about 4 mils. Coating cracked from substrate during
            sectioning.

Silicide-base coatings applied by pack cementation evolved for more extensive study after a brief experimental survey of several materials and techniques. Several variables in the pack-cementation method have been found to affect the life of the resultant coating system; some of these were discussed briefly under Preparation of Coating Systems. Addition of modifying elements to the basic siliciding pack and changes in substrate composition have been found to produce profound changes in the mechanism and degree of protection achieved. This work is still in progress, and reference should be made to the final report on the program for a full account of the findings by Klopp, Maykuth, and Ogden.

The effect of substrate composition on the mechanism of protection is shown by Figures 74 and 75. Siliciding of tantalum produced a coating, thought to be TaSi$_2$, which did not form a truly protective oxide film on the surface, but rather allowed controlled but continuous oxidation of the coating. In contrast, siliciding a Ta-30Cb-10V substrate produced a coating which, during oxidation, formed a thin protective glassy film that gave a sound protective mechanism and prevented continued destruction of the coating via oxidation. A similar effect was observed with a Ta-10Hf-5W substrate with a silicide coating containing a small amount of aluminum. Interdiffusion between the coating and the substrate at high temperatures was found to occur in silicide coated tantalum as shown in Figure 76.
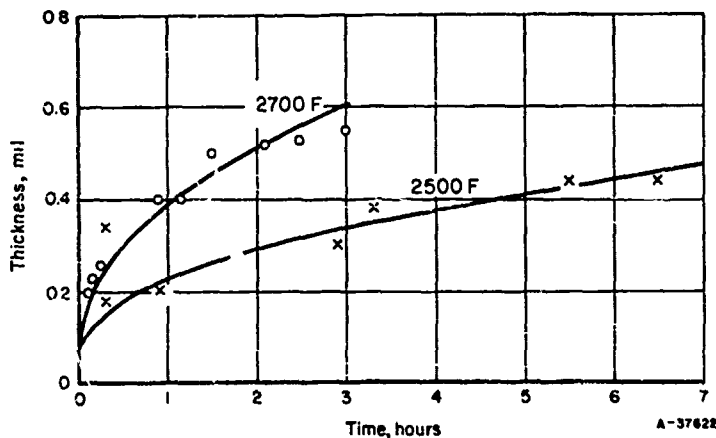
FIGURE 76. GROWTH OF SUBSILICIDE LAYER DURING EXPOSURE TO AIR OF SILICIDE-COATED TANTALUM AT 2500 AND 2700 F

Initial thickness of subsilicide is 0.08 mil.

Modification of silicide-base coatings by deposition of boron or manganese followed by siliconizing has given superior oxidation protection. The most promising coating to date in this program is a coating formed by depositing manganese by pack cementation followed by siliciding, also in a pack. The coating formed in this manner on tantalum gave excellent protection at 2700 F for 24 hours, via glass formation, in isothermal testing with no visible sign of the beginning of failure. The substrate retained a 0 T bend ductility after exposure.

Comparative evaluation of silicide, aluminum-modified silicide, and manganese-modified silicide coatings on tantalum, Ta-10W, Ta-10Hf-5W, and Ta-30Cb-7.5V is in progress. The evaluation includes static, cyclic, and defect testing over the range 1200 to 2700 F.

Chromalloy Corporation. [226c] Silicon-base coatings have protected tantalum for at least 1 hour at 2700 F. As was the case for columbium, embrittlement of the substrate has been a problem with the currently applied techniques.

Fansteel Metallurgical Corporation. [254] Coatings were applied to unalloyed tantalum and to Ta-10W by siliciding from the gas phase, using induction heating, either the substrate (giving a "conversion" coating) or a previously applied coating of molybdenum on the substrate (giving a "duplex" coating), as described previously for columbium.

The coatings obtained were less effective in protecting tantalum and Ta-10W than they were for the columbium substrates studied. It was proposed that the rates of oxidation were lower on columbium than on tantalum due to lower diffusion rates. Reported "lifetimes" to uniform failure were as follows for 1.5 to 2-mil coatings:

Substrate	Coating	Lifetime to Uniform Failure at 2300 F, hr
Ta	Conversion	<1
	Duplex (MoO$_3$ vapor treated)	6
Ta-10W	Conversion	15

Coatings With Other Base Classifications and Unclassifiable Coatings

Data reported by Huminik[185] of Value Engineering for cermet-type coatings on tantalum, applied by electrodeposition techniques involving simultaneous electroplating and electrophoretic processes, are given in Table 45.

Withers[226c] of the American Machine and Foundry Company reported the following results for diffusion-coated tantalum processed by pack cementation:

Coating	Protective Life at 2500 F, hr
Amfkote-3	275
Amfkote-4	312

These coatings are said to be less resistant to thermal shock than is Amfkote-2, developed for molybdenum, and Ampfote-4 is said to have self-healing characteristics.

TABLE 45. CHROMIUM-ZIRCONIUM OXIDE AND CHROMIUM-ZIRCONIUM BORIDE COATINGS FOR TANTALUM[185]

Specimen	Coating Thickness, mils	Time to Failure in Flame Test[a], seconds	Oxidation Screening[b], 1 Hr at 2000 F	Therma. Shock[c]
		Chromium-Zirconium Oxide		
O	3.15	400	No failure	No failure
P	3.20	375	Ditto	Ditto
Q	3.14	365	"	"
R	4.79	450	"	"
		Chromium-Zirconium Boride		
E	2.57	1200+	No failure	No failure
F	3.15	1450	Ditto	Ditto
G	2.14	1350	"	"
H	1.98	1175	"	"

(a) Conducted on specimens 0.062 inch thick x 0.5 inch wide x 2.5 inches long. Specimen temperature maintained at 3800 F. Corrections for emittance nd heat loss were considered in reported temperature. Flame chemistry was oxidizing.

(b) Electric-furnace heating.

(c) Test consisted of cooling specimen to 0 F and then submitting it immediately to the flame test until specimen was uniformly heated to 3860 F. This was followed by an immediate quench in cold water. Considered to be more severe test than actual rocket firing.

COATINGS FOR TUNGSTEN

Coatings for Tungsten

The status of protective coatings for tungsten is not nearly so well advanced as for the other three principal refractory metals. There are two reasons for this. First, efforts have not been as heavily concentrated in this area. Secondly, protection requirements call for service temperatures upwards from 3000 or 3300 F, and all of the problems encountered in protecting the other refractory metals at lower temperatures become magnified by these higher temperatures.

Metallic Coatings

Goetzel, Venkatesan, and Bunshah[46] briefly investigated rhodium plate over tungsten. Brittleness of the coating coupled with thermal-expansion mismatch were problems.

Introduction of intermediate layers was done with the aim of providing better accommodation for the expansion mismatch, and also possibly to promote formation of liquid phases for defect tolerance.

A multiple coating consisting of a first inner layer of chromium, a layer of silicon, a second layer of chromium, and a thin layer of rhodium after heat treatments protected thoriated tungsten at 3000 F for periods up to 20 minutes with self-resistance heating.

Silicide-Base Coatings

W-2 Processed 50W-50Mo. Chromalloy Corporation recently reported that a 50W-50Mo alloy coated by the W-2 process survived over 60 hours at 2700 F.[226c]

New York University. As a continuation of the work on rhodium-plated tungsten, Goetzel and Landler[47] studied silicide-coated tungsten with a target of 10 hours of protection at 3300 F.

Several techniques for siliciding were considered, and the pack method was chosen as the most practical, as well as the one giving the most reliable and reproducible results. Temperature, time, and especially pack composition were found to be variables affecting the integrity of the WSi_2 coating. Figure 16, presented earlier, shows some of these effects on coating thickness. Highest integrity, coupled with a thickness of about 1.5 mils of coating, was obtained with packs containing 10 per cent NaF, 5 per cent NH_4Cl, semiconductor-grade silicon powder, and no inert filler, and a siliconizing cycle of 4 to 8 hours at 1850 to 1950 F.

Pack-siliconized tungsten wires, tested with self-resistance heating, were capable of withstanding oxidation at 3300 F for periods of various duration up to and exceeding 10 hours. Failures could be grouped into three categories, namely, pinhole defects in the coatings, formation of a low-melting phase, and the so-called "disilicide pest". Pinhole failures were observed to occur when the external glass coat formed during the oxidation test was too thin to cover the pinhole or imperfection in the coating sufficiently to prevent oxidation of the substrate and escape of the highly volatile WO_3. The formation of a liquid phase at 3300 F indicated the possible existence of a ternary eutectic in

a W-Si system with another impurity such as oxygen, nitrogen, or a metallic element contained in the silicon of the pack. The WSi_2-W_3Si_2 eutectic is reported to melt only at 3700 F. The disilicide pest, subject of extensive study by several investigators in the case of molybdenum, was found in a series of special experiments to be a manifestation of a low-temperature oxidation of tungsten before effective sealing of the WSi_2 layer, through dense oxide or glassy conversion coatings could be achieved.

The available experimental evidence points to good houskeeping as the most effective way of reducing the frequency and effectiveness of the first and second type of failures.

The third type of failure, disilicide pest, represents a serious shortcoming in the unmodified WSi_2 coating. This occurred in parts exposed to temperatures between 1200 and 2280 F for prolonged periods. It caused a destruction of the disilicide layer over a period of 5 to 15 hours, depending on the coating thickness. With the self-resistance heating method, which was used, the grip ends were kept cold, and therefore areas of the coated specimens were within the pest temperature range. This was the actual life-determining factor in tests where other failures caused by improper preparation techniques had been eliminated.

Coatings up to about 2 mils thick formed glassy layers which generally did not crack during cooling. WSi_2 coatings which were thicker than about 2 mils always exhibited cracks during the rapid temperature changes encountered in cooling from 3300 F.

After 10 hours exposure at 3300 F, 1.5 to 2-mil coatings of WSi_2 were completely converted to W_3Si_2, with a protective glassy layer on top, due to interdiffusion with the tungsten substrate.

Preliminary attempts to deposit ZrO_2 on top of siliconized wires by means of plasma-arc-spray method remained largely unsuccessful because of poor adhesion. Where bonding was obtained, no improvement in life under high-temperature oxidizing conditions could be ascertained.

General Telephone and Electronics Laboratories. An Air Force-sponsored program[50] is currently in progress at GT&E to define and evaluate those variables which are the determining factors in protecting tungsten from atmospheric conditions above 3000 F.

In conjunction with this program, silicide-base coatings on tungsten have been selected, on the basis of preliminary screening tests, for intensive study.[189]

Pack cementation is the principal method of coating preparation. Samples of tungsten to be coated are outgassed in vacuum at 1830 F after pickling in an HF-HNO_3 acid mixture to remove any surface contamination. Typical specimens coated are 0.040-inch-diameter tungsten rods in lengths of about 3 to 3-1/2 inches. These tungsten rods are packed in a mixture consisting of 90 per cent, 325-mesh silicon powder and 10 per cent sodium fluoride. A v. eous-silica tube is used as a container with each end plugged with Fiberfrax insulation. This tube is then placed within a Globar furnace in dry hydrogen and heated at 1920 F for times up to 16 hours. Approximately a 4-mil coating is obtained in 16 hours. The majority of tests have been carried out on coated 0.040-inch-tungsten rods, heated by self-resistance to failure under static conditions. A few cycling tests were made with greatly shortened lifetimes. Under usual test

conditions, temperatures vary from the apparent test temperature at the center of the specimen to about 400 or 570 F at the water-cooled grips.

It soon became clear that, except at the highest test temperature 3304 F, failure usually occurred in the low-temperature region of the specimens. at temperatures between 2190 F and 2460 F. Goetzel and Landier[47] earlier reported a disilicide pest range from 1200 to 2280 F. It has been found possible to extend substantially low-temperature life by modifying the silicide coatings. At 3304 F failure occasionally occurred in the center of the specimens, and examination of the specimens after failure revealed craterlike eruptions in the clear glassy oxide coating, suggesting the remnants of broken bubbles. Tests attempted at temperatures above 3304 F failed, either through eutectic melting of the coating or through pronounced bubbling of the coating.

A real variable affecting specimen life has been the thickness of the coating. Even in specimens that failed by pest formation, the rate of oxidation appeared to be diffusion controlled. Table 46 shows the average test lives observed of silicide and two modified-silicide coated 40-mil-diameter tungsten rods.

TABLE 46. TEST-LIFE RANGE OF SILICIDE COATINGS ON 40-MIL DIAMETER TUNGSTEN ROD[189]

Temperature		Coating Thickness, mils	Oxidation Time, hours		
C	F		Si	Si-"A"	Si-"B"
1095	2003	1	1.5 - 3	5.5	6
		~2	6.5 - >10[a]	--	>10
		3 - 4	8 - >10	>10	--
1370	2498	1	0 - 2.5	0 - 6	6
		~2	0 - >10	--	>10
		3 - 4	7.5 - >10	>10	--
1650	3002	1	0 - 1.5	1	7
		~2	4 - 5	--	6 - 26
		3 - 4	6 - 9	>10 up to 26	--
1818	3304	1	0 - 7.5	0	4.5
		~2	4 - 7	--	>10
		3 - 4	0 - >10	>10	--

(a) >10--Test terminated after 10 hours - specimen intact.

University of Illinois.[48,49,158] As part of a more extensive investigation on ceramic-type coatings, Bergeron et al. examined WSi_2 coatings on tungsten. It was found in some tests that the coatings provided good protection from oxidation for periods up to 10 hours by way of formation of a protective layer of vitreous SiO_2. Disilicide pest also was encountered in this work.

The reliability of these coatings was poor because cracks which were frequently present in the coating exposed the tungsten to air, and rapid oxidation occurred. The

reliability of the coating was reported to be vastly improved by duplexing siliconized specimens with a zircon-glass coating.

Oxide-Base Coatings

Thompson Ramo Wooldridge, Inc., has a current Air Force-sponsored program[51] on the development and evaluation of coatings for the protection of tungsten from oxidation at temperatures in excess of 3300 F. The cl t of materials reported to be of primary intere· · :s the complex oxides.

Members of the Department of Ceramic Engineering at the University of Illinois conducted a broad investigation of ceramic coating systems for the protection of tungsten at 3000 F.[48,49,158] Included in the investigation were WSi_2 coatings as indicated above, ceramic crystals in a glass matrix, zirconia-clad coatings, vapor-deposited SiO, and other combinations of metal, ceramic crystals, and glass coating systems. The coating system considered to be the most protective of those studied was one consisting essentially of 35 per cent glass and 65 per cent zircon.

The procedure used in preparing this coating on tungsten was as follows:

(1) Degassing of tungsten in vacuum (5×10^{-5} mm Hg)

Temp, F	Time, min
3000	5
3500	5
3800	5

(2) Brushing of milled slurry onto tungsten wire and air drying

(3) Firing

Temp, F	Time, min	Atmosphere
1900	1	Vacuum, 2×10^{-5} mm Hg
2150	5	Ditto
2400	3	"
2600	2	"
2850	2	Argon pressure slightly >1 atm

Three separate coating applications involving Steps (2) and (3) were made to insure uniformity and continuity. Thickness of the resulting coatings was 6 to 8 mils.

The coating system maintained oxidation resistance for 10 hours at 3000 F (optical, 3150 to 3200 F true temperature) with muffle heating. The zircon-glass coating converted to monoclinic zirconia and glass after long periods of time at 3000 F.

The mechanism of failure or degradation of this type of coating appeared to be due to a gradual migration of oxygen through the coating to the tungsten, where various tungsten oxides were formed. These oxides then migrated to the coating surface and volatilized.

Cermet-Type Coatings

Results reported by Huminik[185] of Value Engineering for cermet-type coatings on tungsten, applied by electrodeposition techniques involving simultaneous electroplating and electrophoretic processes, are given in Table 47.

<div align="center">

TABLE 47. CHROMIUM-ZIRCONIUM OXIDE AND CHROMIUM-ZIRCONIUM BORIDE COATINGS FOR TUNGSTEN[185]

</div>

Specimen	Coating Thickness, mils	Time to Failure in Flame Test[a], seconds	Oxidation Screening[b], 1 Hr. at 2000 F	Thermal Shock[c]
		Chromium-Zirconium Oxide		
S	3.30	425	No failure	No failure
T	4.63	475	Ditto	Ditto
U	4.61	470	"	"
W	4.64	510	"	"
		Chromium-Zirconium Boride		
I	3.15	1600+	No failure	No failure
J	3.30	1775+	No failure	No failure
X	Specimen damaged in preparation			
Y	Specimen damaged in preparation			

(a) Conducted on specimen 0.062 inch thick x 0.5 inch wide x 2.5 inches long. Specimen temperature maintained at 3800 F. Corrections for emittance and heat loss were considered in reported temperature. Flame chemistry was oxidizing.

(b) Electric-furnace heating.

(c) Test consisted of cooling specimen to 0 F and then submitting it immediately to the flame test until specimen was uniformly heated to 3660 F. This was followed by an immediate quench in cold water. Considered to be more severe test than actual rocket firing.

Coatings for Vanadium

Relatively little effort has been put into the development of protective coatings for vanadium-base alloys.

The Naval Research Laboratory[270] briefly explored the potential of the zinc coating for protecting V-50Cb-5Ti and V-20Cb-5Ti. The nature and performance of the zinc coating on columbium was discussed previously. Results from these studies can be summarized as follows:

(1) Both alloys developed an intermetallic coating on dipping in zinc at 1080 F.

(2) A diffusion anneal in air at 1400 F was more satisfactory than the usual 1600 F anneal given to zinc-coated columbium-base alloys. The lower temperature anneal was a necessity in the case of V-20Cb-5Ti.

(3) In the absence of sizable flaws, the coated V-20Cb-5Ti alloy was oxidation resistant for at least 24 hours at temperatures including 1600 F but less than 1800 F. The coated V-50Cb-5Ti alloy withstood 24 hours at temperatures including 1800 F but less than 2000 F.

(4) When sizable flaws were present, neither of the coated alloys was healed effectively at temperatures of 1600 F or higher. At lower temperatures, an oxide covering developed over the flaws and at least a measure of protection seemed to be conferred.

Klicker and Bomberger[19], of the Crucible Steel Co. of America, under Air Force contract, attempted to protect vanadium sheet from oxidation by coatings prepared from oxide combinations with V_2O_5. The coatings were prepared by mixing the appropriate amount of oxides with a resin binder and sufficient trichloroethylene to give the proper consistency for dipping. Twenty-eight of the more refractory oxide combinations with V_2O_5 were applied to vanadium sheet, but they appeared to offer little protection as coatings.

A program currently is in progress at the Armour Research Foundation under sponsorship of the Navy Bureau of Weapons to develop coatings for protection of vanadium-base alloys.[238]

CURRENT STATUS OF PROTECTIVE COATINGS

Applications and Environments

There are many types of hardware and applications for which it is desirable to use coated refractory metals. Two general areas of application of particular interest at the present time are (1) gas-turbine technology[43,179,278,279] and (2) space-vehicle technology. The former provided the major initial motivation for research and development on protective coatings; and the latter has become the focus of attention and probably will continue to be in the foreseeable future. A third area, that of nuclear-energy applications, is not so well defined in the open literature because of security restrictions; but it is believed that present time-temperature-enthalpy-mass flow requirements are similar to those for currently desired gas-turbine technology.

As previously indicated, there has been a continuing desire to increase the operating temperatures for gas turbines. It appears probable that any major increase in temperature can only be brought about through the use of refractory metals with reliable protective coatings. Turbine buckets (rotor vanes) experience the most severe combination of temperature and stress of any of the turbine parts. They must withstand very high centrifugal as well as superimposed vibratory stresses at elevated temperatures. In addition, they must withstand the blast of hot gases with entrained corroding, impacting, and eroding materials. Also, they must exhibit good resistance to thermal shock and thermal cycling. Much work has been done to provide reliable coatings for molybdenum and, it is believed, columbium alloys for turbine-bucket use. There is not now known to be a gas turbine operating with refractory-metal buckets. Time-temperature requirements to make such a turbine practical are believed to be 50 to 100 hours at 2000 to 2500 F with allowance for about a 300 F transient overtemperature.

The major emphasis at the present time on developing protective coatings for the refractory metals is oriented toward space-vehicle applications. Environmental factors and operating requirements for these applications, where known, have been reviewed by several people[147,179,180,226,280-291].

Figure 77, prepared by Pellini and Harris[290], gives a generalized orientation of the various types of space vehicles. The vertical dotted line at about t = 4 minutes separates (generally) pulse heating and steady-state heating conditions. The lines defining the vehicle zones are not rigid boundaries but indicate generally expected locations. The upper half of the various zones may generally be considered as relating to stagnation points, and the lower half as relating to the 1-foot back positions. The chart also broadly separates vehicles by nature of their flight. Drag re-entry vehicles are grouped in the upper left corner. Thrust flight vehicles, noted on the chart as "Defensive Missiles", are grouped in the lower left-hand corner. Lift flight vehicles, including the cruise and glide subdivisions, are grouped in the right side of the chart. The aerodynamic heat-flux inputs for the lift flight systems, represented on the chart by "Space Re-entry Glide", may exceed the melting point of any known material. This limit is noted by the horizontal dotted line marked "Limit of Fixed Wall". The heat input limits for the drag re-entry class of vehicles might extend to over 10,000 Btu/(sq)(ft)(sec).
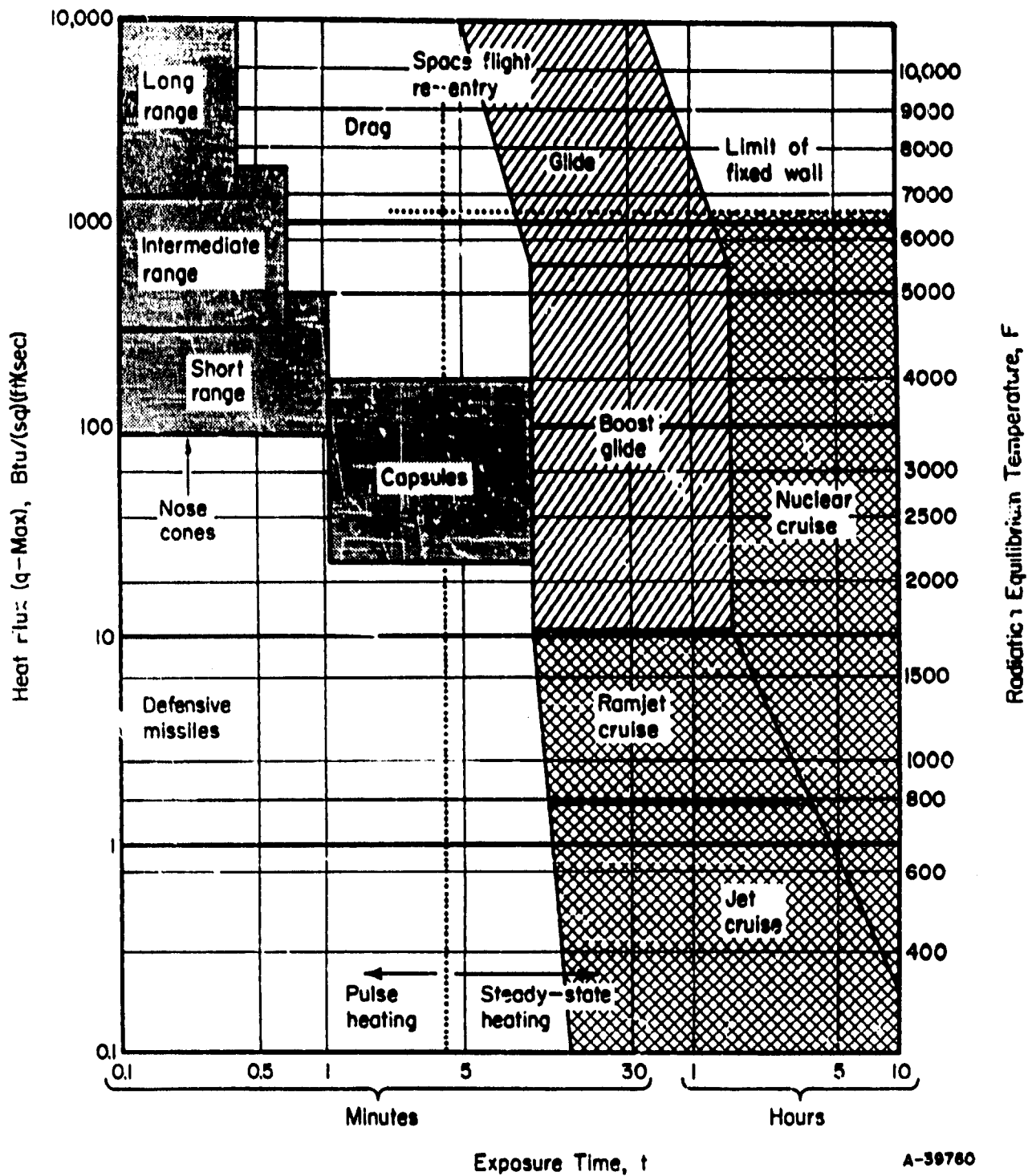
FIGURE 77. THE ENVIRONMENTAL CONDITIONS OF VARIOUS CLASSES OF VEHICLES UNDER CONDITIONS OF STEADY-STATE HEATING (RIGHT) AND PULSE HEATING (LEFT)[290]

The lines defining the vehicle zones are not rigid boundaries but indicate generally expected locations.

Table 48, reported by Walton[286], gives approximate environmental conditions for various applications of high-temperature coatings. A similar type of listing, but varying in some of the values of the parameters, is presented in Table 49, which was reported by Sterry[281]. Table 50 is a partial listing of the material requirements for glide re-entry vehicles reported by Braun[281].

TABLE 48. APPROXIMATE ENVIRONMENTAL CONDITIONS FOR VARIOUS APPLICATIONS OF HIGH-TEMPERATURE COATINGS[286]

Variable[a]	Applications			
	Ballistic Nose Cone	Leading Edge	Ramjet	Domes
Time, min	0.5-2	30-120	1-240	30-120
Surface Temp, F	2500 to ablating	2500-5000	2500 to ablating	2500 to ablating
Max Particle Velocity, ft/sec	2500	2200	1000	2500
Gas Enthalpy, Btu/lb	6000-9000	7000-10,000	500-2000	6000-10,000
Heat Flux, Btu/(ft^2)(sec)	200-4000	10-300	3-100	10-500
Gas Composition	Air (dissoc.)	Air (dissoc.)	Combustion Atmosphere	Air (dissoc.)
Mass Flow, lb/(ft^2)(sec)	1000	1000	10-150	1000
Temperature Programming, sec[b]	0.1-0.5	600-6000	15-30	0.1-60
Pressure Programming[c]	10^{-3} to 29.9 in. Hg	10^{-3} to 29.9 in. Hg	1 to 3 atm in 15 sec	10^{-3} to 29.9 in. Hg
Cyclical Operation	No	Yes	Yes	Yes
Specimen Configuration	Cones Plates	Cylinders Cones Plates	Cones Plates	Cones Plates

(a) Numbers are only approximate and represent no actual present or future application exactly.

(b) Time to reach maximum temperature.

(c) Range of pressure which can possibly be achieved in a realistic experiment and not actually encountered.

TABLE 49. HIGH-TEMPERATURE COMPONENT ENVIRONMENTS[281]

Component	Max Heat Flux, Btu/(ft^2)(sec)	Stagnation Temperature, F	Time/Cycle, min	Atmosphere
Nosecaps (ballistic re-entry)	200-4000	3000-14000	0.5-2	Oxidizing
Nosecaps (glide re-entry)	100-300	3000-6000	10-90	Oxidizing
Leading edges (glide re-entry)	20-60	1800-3000	10-90	Oxidizing
Skin panels (glide re-entry)	10-25	1500-2500	10-90	Oxidizing
Ramjet liners	10-300	2000-5000	1-120	Oxidizing and reducing
Rocket nozzles and jetavators	2000-4000	4000 to 5500 eventually 7000 F	0.05-4	Oxidizing and reducing

TABLE 50. PARTIAL LIST OF MATERIAL REQUIREMENTS FOR GLIDE RE-ENTRY VEHICLES[281]

Nose Cap and Leading Edges.

1. High Melting Point

   6000 F nose cone
   4000 F leading edge

2. Oxidation resistant: no catastrophic alteration for 1 hour at the above temperatures

3. Erosion resistant up to 35,000 fps

4. Thermal shock resistant for $\Delta T = 100$ F/sec

5. High radiating surface: high emissivity, $E \approx 0.9$

6. Suitable attachment method

Primary Structure and Skin Panels

1. High strength-to-weight ratios at service temperatures up to 3600 F

2. Oxidation resistant: no catastrophic alteration after 8 hr at 3000 F

3. Erosion resistant up to 35,000 fps

4. Low thermal expansion

5. High radiating surface: high emissivity, $E \approx 0.9$

6. Weldable

7. Suitable for attachment of mechanical fastenings

Mention was made earlier in this report of the importance of considering emissivity in coating systems. Figure 78 shows the significance of this aspect.

Status of Coating Systems

The status of coating systems involving the four principal refractory metals can best be presented at this time from the standpoint of three different temperature-time applications as follows:
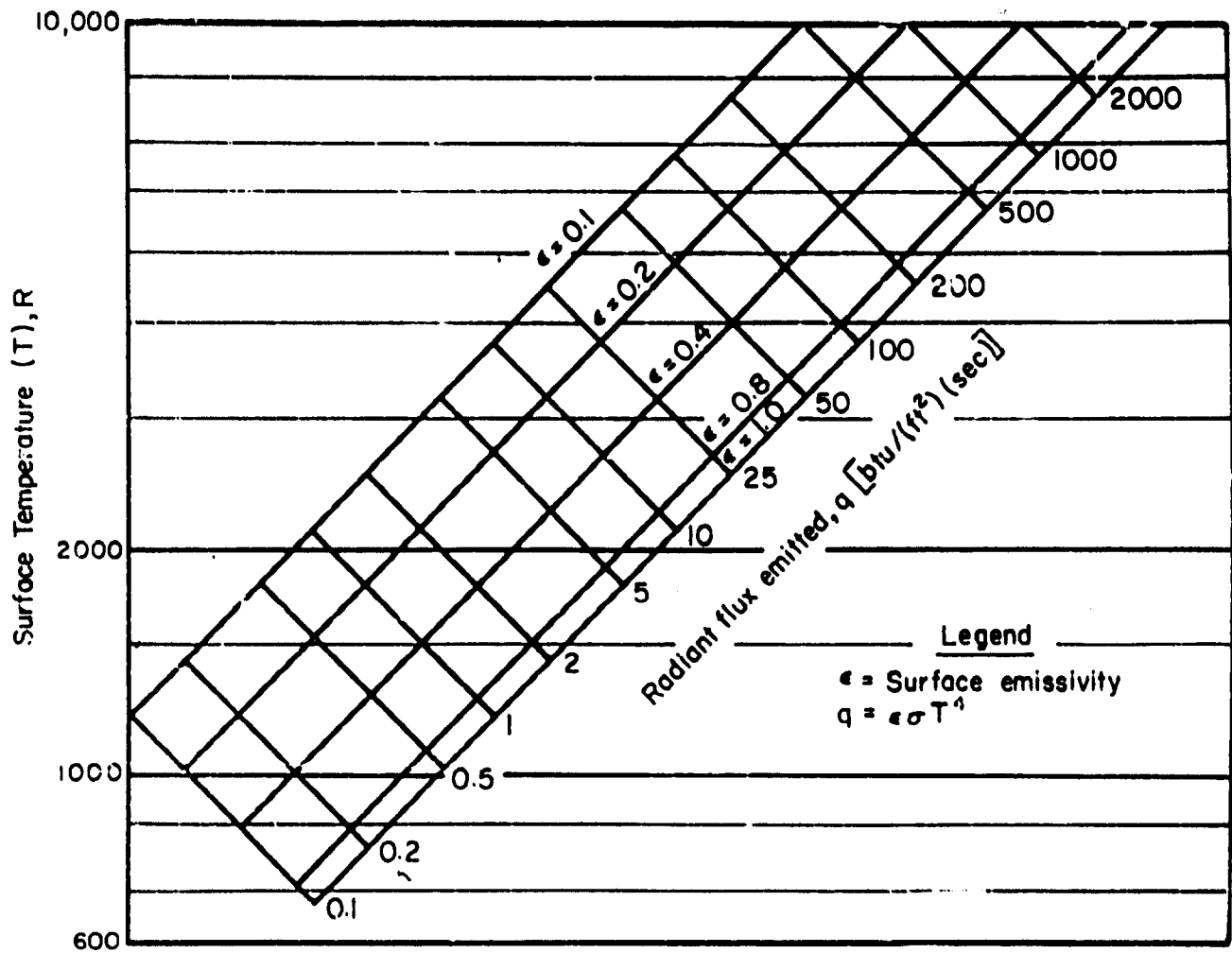
FIGURE 78. THERMAL RADIATION HEAT FLUX RATE AS A FUNCTION OF SURFACE TEMPERATURE AND EMISSIVITY[282]

Coating Class	Temperature, F.	Time, hr	Application
I	2000-2500	50-100	Turbojet
II	2500-3000	Up to several	Ramjet, re-entry vehicles
III	Over 3000	Up to several	Superorbital vehicles

Each coating class can be further broken down into "promising" and "interesting" systems. A promising system is defined as one which appears to have potential for accomplishing a class of mission based on the evaluation results obtained from more than one source. An interesting system is defined as one which appears to have the potential for accomplishing a class of mission based on the evaluation results from only a single source.

The itemized breakdowns are as follows:

Class I Coatings (2000-2500 F, 50-100 Hr)

Substrate Base	Promising Systems	Interesting Systems
Mo	Sprayed Al_2O_3 over Cr plate	--
Cb	--	Glass impregnated Al_2O_3, sprayed
Ta	--	--
W	--	--

Class II Coatings (2500-3000 F, up to Several Hours)

Substrate Base	Promising Systems	Interesting Systems
Mo	(1) Silicide + additives, pack cementation (2) Sprayed Al_2O_3 over Cr plate	(1) Pt, electroplated (2) Al-Si, sprayed
Cb	(1) Aluminide + additives, various methods (2) Cr-Ti + Si, vapor diffusion, modified pack cementation (3) Silicide + additives, pack cementation	-- -- --
Ta	-- -- --	(1) Aluminide + additives, various methods (2) Silicide + additives, pack cementation (3) Beryllide, vapor diffusion
W	-- --	(1) Silicide + additives, pack cementation (2) Zircon + glass, paint and sinter

Class III Coatings (Over 3000 F, up to Several Hours)

Substrate	Promising Systems	Interesting Systems
Mo	--	--
Ta	--	--
W	--	Silicide + additives, pack cementation

The pack-cementation and the paint (slurry dip, spray, or brush) and diffuse techniques appear to offer the greatest potential at the present time for producing coated hardware involving complex geometry. Noteworthy coating systems have been produced by hot-spraying techniques, but these methods of application have been limited to relatively simple geometry.

The present status of protective coatings for refractory metals must be termed predominantly one of research and development. Coatings for molybdenum have been under investigation for the longest period of time and have received the most attention. Some of these currently are commercially available. Substantial progress has been made during the past 2 years on coatings for columbium and tantalum. Because tungsten will find its major role in applications at temperatures over 3000 F, and because less work has been done on coatings for tungsten than for the other metals, much additional research and development work remains to be done before practical hardware will be a reality.

Many problems remain unsolved and, as the current research and development programs progress, new problems will be uncovered. All of these problems must be attacked by sound research programs if the refractory metals are going to be reliably protected from oxidation, and thus find their role as structural materials.

Problem Areas

Research and development programs on protective coatings frequently take considerable time before they proceed from simple static oxidation testing to advanced evaluations under simulated service environments. Among the problems frequently encountered are: (1) thermal-expansion mismatch, (2) pinholes, (3) difficulty of corner, edge, and recess protection, (4) poor bonding, (5) excessive diffusion, (6) interconnecting porosity, (7) brittleness, (8) lack of defect tolerance, and (9) low-temperature pest failures.

The primary needs in the protective coating of refractory metals are:

(1) New concepts for coating systems and methods of preparing coating systems

(2) Systematic data on effects of processing variables in coating systems

(3) Target properties for use by coating producers

(4) Fundamental data on composite material properties such as diffusion rates, bonding, mechanical compatibility, and pertinent phase equilibria

(5) Information on detailed mechanism of failure in various coating systems

(6) Reduction of brittleness in coating systems

(7) Improved defect tolerance in coating systems and better quantitative standards for defect tolerance (self-healing)

(8) Uniform and discriminating evaluation procedures for various applications

      (a) Screening

      (b) Simulating service

(9) Elimination of degradation of substrate properties due to coating process and/or presence of coating

(10) Procedures for coating structures joined mechanically

(11) Improved reliability of coating systems

      (a) Adequate inspection procedures

      (b) Better procedures for estimating reliability levels

(12) Adequate repair methods

(13) Better coating systems with promise for Class I service

(14) Better coating systems for Class III service.

Philosophy of the Development of Protective Coatings

The general problem of protecting the refractory metals from oxidation can be broken down into two major subproblems:

(1) Finding coating materials which have the required oxidation resistance in their own right and which have the required chemical, physical, and metallurgical properties to be compatible with the substrate alloy to be protected

(2) Developing a process for putting the coating material and the alloy substrate together into a workable system which will reliably accomplish a specified mission.

The history of coatings research and development has shown that neither of these problems is simple and easily solved. Yet we have good reason to believe that the problems are solvable.

There is not now and probably never will be a universal coating that will provide oxidation resistance to all structural refractory-metal alloys in all of the contemplated applications. Hence, early in any research program, it is important to specify the exact alloy substrate to be protected and the geometry of the hardware to be used. It is likewise very important to specify the exact environment in which protection must be achieved. These specifications set limits or boundaries to the over-all problem and allow the research worker to classify materials roughly as potentially promising or not promising as coatings. The specifications also permit the establishment of realistic evaluation procedures for judging the merits of different coatings.

Realistic evaluation is necessary because, if the testing conditions are more severe than the intended service conditions, some useful systems for solving a particular problem may be overlooked. On the other hand, if the test conditions are less severe than those of the service environment, as is most frequently the case, coating systems could well be carried through needless and costly development programs which would not contribute to the solution of the particular problem at hand.

Some of the properties considered in selecting potential coating materials are: oxidation resistance, thermal-expansion characteristics, elastic modulus, thermal conductivity, tensile or fracture strength, stability toward chemical reaction and inter-diffusion with the substrate, thermal-shock resistance, and gaseous-transport characteristics.

Although each application for a coated system has its own set of environmental factors, coated systems generally must be evaluated with respect to one or more of the following conditions: tension, compression, impact, fatigue, creep, bending, vibration, shear, elongation, thermal shock, erosion, hypersonic air flow, notch sensitivity, and defect tolerance. Also, in re-entry applications, the emissivity of the coated system can be of major importance.

After a good coating system has been produced, there remain problems of education of personnel, inspection, and repair. Coated systems, in general, do not withstand much physical abuse, and a special educational program is frequently required for production personnel. Even with special educational programs, coated systems may suffer damage or be produced with flaws. Reliable nondestructive test methods are urgently needed in the current state of the art of protective coatings for the refractory metals.

Recommendations

(1) Protection of the refractory metals from oxidation should be viewed as a major materials problem.

(2) In view of the progress which has been made by the empirical approach to date, and in view of the urgency of solving current problems, some of this type of approach should be continued. Programs of this nature should be oriented toward providing protection to a specific realistic

substrate composition and configuration to be used in accomplishing a specific mission.

(3) It is believed that the empirical approach to the over-all problem is rapidly reaching the point of diminishing returns. Silicide-base and aluminide-base coatings applied by pack cementation are reaching the point where some research and development efforts are being duplicated without producing any major advances in the state of the art. An integrated program should be carried out for the purpose of identifying the fundamental factors and properties which are necessary to produce a reliable coating system.

(4) Most current coating systems do not fail uniformly. Rather, they fail at randomly located areas which frequently are not centers of macroscopic stress concentration. It is believed that the performance of current systems could be improved by research to identify the causes of such random failures, and that such a program is vitally needed if the long-term requirements for protected refractory metals are to be met.

(5) Most programs on the development of protective coatings have striven for "oxidation resistance" without much concern for the relative mechanical and thermophysical properties of the coating and substrate. There is substantial experimental and theoretical evidence that these properties are of great importance to the performance of a coating system. Once a substrate has been selected, its properties are relatively fixed. A long-range research program should be carried out with the objective of finding ways of adjusting the mechanical and thermophysical properties of known oxidation-resistant materials to better natch those of the substrate without impairing the inherent oxidation resistance.

(6) Of vital importance is the establishment of a set of standardized realistic evaluation procedures for different classes of missions, not only for coating systems which have reached an advanced status, but also for screening purposes in small-scale research investigations. Action in this area is needed to bring some order into a field of technology which currently has much chaos.

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157	A Summary of the Theory of Fracture in Metals, August 7, 1961
158	Stress-Corrosion Cracking of High-Strength Stainless Steels in Atmospheric Environments, September 15, 1961
159	Gas-Pressure Bonding, September 25, 1961
160	Introduction to Metals for Elevated-Temperature Use, October 27, 1961
161	Status Report No. 1 on Department of Defense Refractory Metals Sheet-Rolling Program, November 2, 1961

Battelle Memorial Institute, Defense Metals
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COATINGS FOR THE PROTECTION OF
REFRACTORY METALS FROM OXIDATION, by
C. A. Krier. 24 November 1961. 226 p. incl.
illus., tables, 291 refs. (DMIC Report 162)
[AF 33(616)-7747]   Unclassified report

The present status of the development of coatings
to protect refractory metals from oxidation is
summarized. The work in progress throughout the
country on this subject, primarily under Govern-
ment sponsorship, is reviewed.

Coatings for molybdenum are most advanced.
Silicide-base coatings capable of meeting at least
limited objectives are available. The protection
of tungsten is of major importance, but no really
satisfactory protection system is yet in sight.

1. Refractory metals –
   Coatings
2. Refractory metals –
   Oxidation
I. Krier, C. A.
II. Defense Metals Information
   Center
III. Contract AF 33(616)-7747